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Final Contract Report

EVALUATION OF ATMOSPHERIC FLASH PYROLYSIS FOR COPROCESSING RESIDUE

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SUMMARY

This report describes flash pyrolysis studies using the Waterloo Fast Pyrolysis Process (WFPP) for two very different feed materials. The Waterloo Fast Pyrolysis Process is an atmospheric pressure fluidized bed technology, originally developed for biomass, but which has been tested extensively on coals also, with results described in previous reports. Based on this earlier work, a series of pyrolysis tests (Part A) was carried out on a Saskatchewan (Coronach) lignite, using a small pilot plant unit with feed rates of 1-2 kg/h of both raw coal and acid-washed coal. The larger pyrolysis unit allowed sufficient liquid to be produced that some fairly extensive characterization tests could be done, by solvent fractionation and by GC-MS. Some pyrolysis tests were also carried out with the fluid bed sand normally used replaced by a catalyst.

A second program (Part B) was carried out in the bench scale continuous fluid bed unit, which normally has a throughput of 15-30 g/h. These tests had as their objective the evaluation of the flash pyrolysis behaviour of heavy residues, specifically those produced from the CANMET coprocessing pilot plant, which is designed to liquefy bitumen-coal mixtures. Whereas the Waterloo pyrolysis group had considerable previous expertise in the pyrolysis of low rank coals, the use of heavy hydrocarbon residues in the WFPP was a new application. Only limited quantities of CANMET

coprocessing residue were available, so the initial experimentation during the learning period was carried out using a vacuum tower bottom residue (Suncor) as the feed material. Also, because the use of higher pyrolysis temperatures than for biomass or coal was of interest, a new bench scale fluidized bed reactor was constructed from Inconel, which allowed pyrolysis temperatures to 900°C to be used.

The principal objectives of pyrolysis tests with lignite were to establish the optimum processing conditions for maximum liquid yields, to assess the quality of the liquid product from raw coal or acid-washed coal, and to determine if the liquid quality could be affected favorably by use of a catalyst in the fluid bed.

The major objective of pyrolysis tests on coprocessing residues was to assess whether a reasonable yield of a fluid oil was obtainable, together with a dry coke of acceptable properties. If both of these ends could be accomplished, the residue pyrolysis process would possess a better degree of economic viability. Given the very large amounts of residues which will be available in the not-too-distant future from newer technology such as coprocessing, hydrocracking, upgrading etc. it would be desirable to recover as much of the pyrolysis products as possible in a commercially attractive form.

Three coals were pyrolyzed in the small pilot plant unit, (raw and acid-washed Coronach lignite and Forestburg subbituminous

coal) and gave tar yields of about 13% to 20%. Raw Coronach lignite with low moisture gave tar yields at the optimum temperature of 650°C of 13.6%. Increase in moisture content from 4% to 9.6% to 22.8% gave increasing tar yields of 13.6 weight % maf to 15.1% to 17.3%, respectively. Higher moisture content acid-washed lignite gave a tar yield of 20.0% with the increased tar yield from 17.3% to 20.0% accompanying a concurrent decrease in gas yield, primarily CO_2. The major effect on the pyrolysis liquids of acid washing of lignite which removes mainly ion exchanged alkali cations, appears to be to preserve the carboxylic acid groups in the volatile product. The effect of moisture content in enhancing tar yields is not understood as yet, but may be related to mass transfer effects in the coal pore structure due to the excess of moisture. Forestburg coal gave a tar yield of 17.2% maf similar to that of the normal lignite (9.6% moisture).

Analyses of the liquid products from the raw Coronach lignite showed that asphaltene and preasphaltene yields were proportional to moisture content, while the oil yield was not affected. In general, solvent fractions were in the order asphaltene > oil > preasphaltene. "Preasphaltene" fractions from lignite contained up to 50% methanol-soluble compounds (up to 2.9% maf coal), and therefore much of the so-called preasphaltenes from lignite pyrolysis are probably not related to polynuclear aromatic compounds. The tar from Forestburg subbituminous coal gave a lower preasphaltene fraction than did the lignite. Acid-washed lignite gave

higher asphaltene yields than did raw lignite, so that the increased tar yield was due almost entirely to increased asphaltene production.

The pentane soluble fraction of a tar from Coronach lignite showed considerable amounts of phenol derivatives, and alkanes and alkenes from C_{14} to C_{26}. The toluene soluble fraction contained substantial amounts of oxygenated aromatic compounds such as phenols, cresols, catechols, xylenol and resorcinol.

Some 20% to 35% of the hydrogen in the original lignite appeared in the tar but only 5% to 13% of the oxygen. Much of the rest of the hydrogen and oxygen appeared as water. Carbon conversion to char increased with temperature, and the carbon content of pyrolysis products increased with temperature in all cases. The H/C atomic ratio of tars decreased steadily with temperature, and the hydrogen content was dependent on the coal and on acid pretreatment. H/C ratio of tars was in the order Forestburg > raw Coronach lignite > acid-washed lignite. A hydrogen rich tar is obtained at lower temperatures, shorter residence time and higher feed rates.

Pyrolysis of lignite in a hydrogen atmosphere reduced tar yields and increased yields of monophenols while decreasing yields of dihydroxybenzenes. The effect of a nickel catalyst was to significantly decrease tar yields, and to decrease the yield of dihydroxybenzenes. Impregnation of lignite with $ZnCl_2$ before

pyrolysis in a sand bed with both nitrogen and hydrogen atmospheres slightly increased conversion of the coal, and increased yields significantly of BTX.

In summary, good yields of tars high in phenolic compounds can be obtained from the pyrolysis of lignites, and yields are enhanced by moisture contents to 22%. Increased yields of BTX appear to be possible using a H_2 atmosphere and a suitable catalyst. Acid washing of lignite increases the tar yield although this increase appears to be due largely to the preservation of carboxylate groups in the tar.

Pyrolysis of coprocessing residues, vacuum tower residue and a low volatile caking bituminous coal (Balmer) was attempted, with the latter two feed stocks being used as simulated coprocessing residue during reactor development studies. The heavy bitumen, or bitumen/coal residues, of which the CANMET coprocessing residue is one example, have the common feature of a highly coking structure, and of passing through a plastic, very sticky, stage before decomposition temperatures are reached. As a result, a strong and highly adherent coke is formed on any surface which the sticky plastic feed encounters. In small laboratory reactors, these characteristics posed severe operating problems because of the small clearances and high surface to volume ratios. Pyrolysis runs which yielded valid data were completed, but run times in the bench scale fluid bed used were shorter than normal (10-20 minutes). Pyrolysis of coprocessing residue in a fluidized bed at

700°C yielded about 50% liquid hydrocarbon (maf basis), 44% char and 6% gas. At 535°C, liquid yield was about 40%.

Because of the severe problems with caking and agglomeration of the sand bed, a modified spouted bed reactor was designed. Better performance and longer runs resulted than for the fluid bed, but runs were still short and plugging could not be prevented. Data was not very consistent due to the erratic behaviour of the bed as agglomeration occurred, which exaggerated the substantial temperature gradients which normally can exist in a spouted bed reactor. However, liquid yields of 55% were obtained at 685°C and 48% at 800°C. Gas yields were respectively 11% and 24% and char yields 32% and 31%. At 685°C the principal gases were C_2H_4 and C_4+ hydrocarbons, and hydrocarbons made up 95% of the gases. At 800°C, the yields of all gases increased, particularly that of H_2 and CO, but hydrocarbon gases still made up 82% of the total gas yield. The reaction of the small amount of water present could account for the increased H_2 and CO at the higher temperature. Clearly, atmospheric flash pyrolysis is capable of giving good liquid yields from a granular coprocessing residue at reasonable temperatures of 650° to 700°C. However, the design of a reactor which can meet industrial scale requirements still has not been settled.

Several trials were carried out using a caking coal with various fluidized bed and spouted bed arrangements, for example,

with alternate feed arrangements, and with an internal draft tube spouted bed. Some improvements in performance were achieved, and by the termination of the contract, some directions for future reactor development had been indicated which might lead to a successful continuous flash pyrolysis process for these difficult feeds. The high level of recovery of liquids and the dry, hard coke produced from flash pyrolysis suggest that such a development would be worthwhile, not only for coprocessing residues, but for other heavy oil residues or for caking coals.

EVALUATION OF ATMOSPHERIC FLASH PYROLYSIS FOR COPROCESSING RESIDUE

1. INTRODUCTION

There are solid arguments that flash pyrolysis is technically and economically the most attractive coal conversion process available. Technically it is one of the simplest and least severe coal conversion processes and thus has low capital costs. The major difference from other coal liquefaction processes is that pyrolysis converts only a limited amount of coal to liquid (rarely above 25%). The largest fraction of the energy input is produced in a solid carbonaceous char and, therefore, the economic viability of the pyrolysis process depends on the complete utilization of the residual char. If an atmospheric pressure, rapid pyrolysis process is combined with a combustion or gasification unit that can utilize the char, then there is potential for the economic production of gaseous and liquid products. For example the liquid and gaseous hydrocarbons could be skimmed off the coal prior to (i) combustion of the char in a thermal generating station to produce electric power or (ii) gasification of the char to produce synthesis gas.

CHRONOLOGY

Work on coal pyrolysis was initiated at the University of Waterloo in 1979 using a small bench scale fluidized bed apparatus patterned after that developed by CSIRO (1). During the initial work carried out (2), a somewhat larger scale reactor was developed than that used at CSIRO - 15 g/hr throughput rather than 1-3 g/hr. This larger scale was made possible by the development of a new entrained flow feeder which allowed feed rates of 5-100 g/hr with a reproducibility of 5 percent (3). In this preliminary work, the methodology and procedures were developed for the bench scale mini-fluidized bed apparatus, and a series of pyrolysis tests were done on Alberta Forestburg subbituminous coal that gave yields of liquids comparable to those obtained by others.

In June, 1981, a new program was initiated to evaluate the short residence time pyrolysis of coal at atmospheric pressure with the primary objective of determining conditions for optimum yields of liquids from a subbituminous coal (4). During this work, covering the period to June 1, 1982, the bench scale fluidized bed method was improved so that better material balances were obtained, and a small stainless steel reactor was developed in place of the earlier quartz version. In fact, three coals were tested for pyrolysis behaviour: two Alberta subbituminous coals, and a Nova Scotia bituminous coal.

Results from this work were sufficiently encouraging that a further program was planned for 1982/83. The results from this program, were given in a previous report by Scott (5). In this work, eight Canadian coals were tested to determine optimal yields of liquids obtainable through flash pyrolysis in the atmospheric pressure fluidized bed process. Although the best tar yields were obtained with strongly caking high volatile bituminous coals, agglomeration in the fluid bed during pyrolysis caused severe operating problems. Pre-oxidation of the coal prevented agglomeration but also adversely affected tar yields. Therefore, further work was proposed to be carried out on lignite and subbituminous coals only.

SUMMARY OF EARLY WORK

Some of the more relevant results from the early pyrolysis studies are given below.

1. The fluid bed flash pyrolysis process exhibits an optimum temperature for maximum liquid yield. This temperature is from 600°-650°C for low rank coals and 650°-700°C for higher rank coals. The maximum tar yield for Canadian bituminous coals can be predicted from the CSIRO correlation of parent coal H/C ratio vs. maximum tar yield. Tar yields from lower rank coals are not yet predictable, and are not related to the volatile yield of a proximate analysis.

2. The tar and char products from low rank coals show a decreasing atomic H/C ratio as temperature increases. The H/C ratios for bituminous coal tars and chars remain reasonably constant with temperature.

3. For both low rank and high rank coals the shortest residence time gave the highest liquid yields (0.2 to 0.45 seconds).

4. The minimum particle size for good liquid yields from fluidized beds appears to be about 100 um. However, this will be a function of reactor configuration, operating mode, and heat transfer capabilities.

5. Accumulation of char in the reactor does not affect liquid yields providing the char is not activated at high temperatures

(above 900°C). The use of a carbon dioxide atmosphere does not appear to improve liquid yields for a coal previously exposed to carbon dioxide. However, a fresh, unoxidized coal might show some effect - this has yet to be determined.

6. The use of a hydrogen atmosphere and a Co-Mo de-oxygenation-hydrogenation catalyst as the fluid bed material did not improve tar yields for lower rank coals. However, catalytic effects were evident, so that a different choice of catalyst might prove to be beneficial.

7. Quenching of the reaction products with a flow of cold gas did not improve liquid yields in this reactor. The reasons are not clear, but may be due to higher gas velocities in the reactor.

8. Acid washing of a lignite to remove cations associated with the organic matter, followed by pyrolysis, gave a dramatic increase in maximum tar yield - about 50 percent. The acid washed lignite gives a tar yield in agreement with that predicted from CSIRO and U.S. results for acid washed lignites or brown coals.

9. Pre-oxidation of a strongly caking bituminous coal prevents agglomeration and caking in the fluidized bed. Without such pretreatment, operating problems due to caking of the bed solids may arise. However, pre-oxidation of the coal also causes a significant decrease in tar yield. Some optimum level of treatment should exist.

10. In general, Canadian coals, especially those from Western Canada, have low H/C ratios compared to coals of similar rank from other sources. Low H/C ratios can be correlated generally to lower tar yields. The highest tar yields were obtained from high volatile bituminous coal, (16-20%), or from acid washed lignite (12-14%). The lowest tar yields were obtained from low volatile bituminous coal, or from high ash sub-bituminous coals (5-7%). The range of tar yields from lignite, sub-bituminous coals, and medium volatile bituminous coals is from 10-14 percent(all yields maf).

11. Chars produced in the pyrolysis process, particularly those formed at the lower temperatures, are very reactive. There is strong evidence that they rapidly adsorb oxygen and water from the air even on short exposure.

12. Studies on pyrolysis of coals should use dry feeds, and chars should be kept in a dry inert atmosphere as much as possible, if good material balances and good analytical results are desired.

13. The fluidized bed reactor appears to be a very suitable device for the pyrolysis of lignite or subbituminous coals. No operating problems were encountered in the bench scale unit and product yields were about the same as those obtained by others. The "blow-through" method of operation used in the Waterloo Flash Pyrolysis Process for biomass appears to be feasible also for low rank coals, so that transport of heat carrying sand is

not necessary and a single fluidized reactor with an independent heat source can be used.

14. Initial results from TGA experiments indicate that heavy residues such as hydrotreater pitch, coprocessing residues, refinery vacuum bottoms, etc. can be pyrolyzed at high temperatures and short times to give substantial oil yields and a dry coke. Adapting the Waterloo Fast Pyrolysis Process, using a fluid bed reactor, to accept such feeds could be a promising area of research.

2. OBJECTIVES OF PRESENT WORK

Results of work carried out by the pyrolysis group in the Department of Chemical Engineering of the University of Waterloo have indicated which Canadian coals are best suited as feedstocks for a flash pyrolysis process; on technical and economic grounds. In this study(Scott,1984), the Saskatchewan lignites, the Alberta subbituminous and the Nova Scotia Devco coals gave the most promising results in terms of liquid yield. The high volatile bituminous coal, however, showed operating difficulties due to its caking properties. In addition, the three coals represent important deposits presently used, or which it is proposed to use, as steaming coals, and therefore a pyrolysis process could be readily coupled to a power generating station using char, gas and coal. This flash pyrolysis scheme represents one of the most economical routes to liquid syncrude production from coal.

Accordingly, the following are the objectives of the present process development program on the production of liquids by flash pyrolysis of coal:

1. Evaluation of liquid yields from a Saskatchewan lignite and an Alberta subbituminous coal as a function of process conditions, on a larger scale than previous work, in a continuous atmospheric pressure fluidized bed flash pyrolysis unit at feed rates from 1 kg/h to 3 kg/h. Quantities of liquid product adequate for several quality tests will be also obtained.

2. Characterization of the liquid product quality in some detail as a function of process conditions, for both coals.

3. Investigation of the effect of acid washing to remove cations associated with the organic matter in Saskatchewan lignite on yields and the chemical nature of liquid products from the pilot plant flash pyrolysis.

4. To investigate further the effect of a catalytic fluidized bed in producing higher grade liquid products in flash pyrolysis, and in particular, to produce a low-oxygen content liquid from Saskatchewan lignite. Initial results with a Co/Mo catalyst show that this process modification is a potentially promising approach.

A second part of the current program of work is concerned with the possibility of using the flash pyrolysis process to convert petroleum residues, or coal liquefaction residues, to useful products. Distillation of heavy crudes or bitumens yields large amounts of heavy residues. Some of this material can be absorbed for asphalt manufacture, but quantities greatly in excess of this use will be available in the near future. Even if the heavy residue is hydrotreated, from 10% to 40% of the feed still is recovered as a pitch. Similarly, coprocessing of bitumen and coal yields a residue for which some use needs to be found. Economic utilization of these residues is a problem which will require some solutions in the near future.

Preliminary thermogravimetric analysis of CANMET coprocessing residues indicated that short time high temperature pyrolysis could lead to significant yields of liquid oils and to a dry coke. Accordingly, a second part of the current contract study had the following objectives.

5. Evaluation of the coprocessing residues from the CANMET bench scale unit as a feedstock for flash pyrolysis. This material is only available from CANMET and samples obtained under different processing conditions were to be supplied, together with data on feedstocks used.

Most of the objectives set out above were achieved, although evaluation of the performance in flash pyrolysis of coprocessing residues was not as extensive as originally envisaged, both because of operating problems with the material as a pyrolysis feedstock, and because only a limited number of samples were available.

3. EXPERIMENTAL APPARATUS AND PROCEDURES

Experiments on coal pyrolysis were carried out in both bench scale (feed rates up to 100 g/h) and a small pilotscale reactor (feed rates up to 3 kg/h). All work on the pyrolysis of coprocessing residues was done using bench scale reactors, either the standard fluidized bed unit, or special modifications of this unit.

PILOT SCALE PYROLYSIS

Pyrolysis runs were performed using the 1-3 kg/h pilot plant unit without major modification to the product collection system.

The process flow sheet for the pilot plant is shown in Figure 3.1. Details of the construction and operation of the unit have been given by Scott and Piskorz (6).

Coal was charged to a hopper equipped with a twin screw feeder and conveyed pneumatically to the fluidized bed reactor. An electrical furnace surrounding the gas inlet line and the plenum chamber supplied most of the heat to the bed of sand. Additional heat was supplied by three electrical cartridge heaters immersed in the bed. During a run char was separated from the volatile products by an insulated cyclone and collected in a cold char pot. The volatile products then passed through a system of two condensers, two separators, and a cotton wool filter connected in series. The temperature in the first condenser was maintained

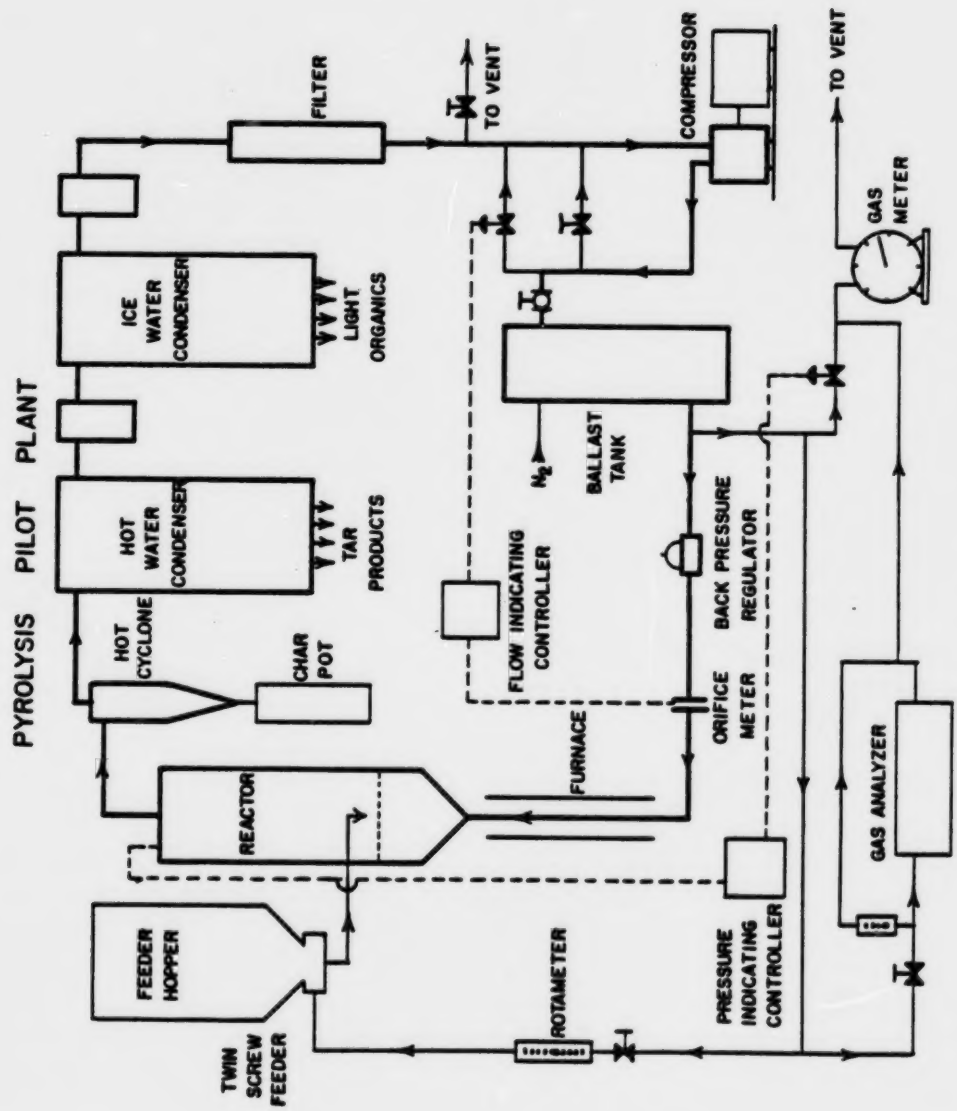


Fig.3.1. Waterloo flash pyrolysis process (pilot plant unit).

by either hot or cold water and could be controlled over the range of about 15° to 50°C. The temperature of the second condenser was maintained by ice water and usually approached 0°C. Four plastic sample bottles were connected beneath each condenser to collect any flowing condensed liquid products. A Schrader bellows pot was connected after each condenser and helped to separate any entrained liquid or solid from the gas stream. Finally a cotton wool filter stopped the remaining tar fog and allowed a fairly clean product gas. A constant system pressure was maintained by venting the volume of pyrolysis gas produced through a gas meter and then through a pressure control valve. An Anarad Infrared Gas Analyzer Series AR-400 gave a continuous reading of CO and CO_2 gas percentages in the product gas. A gas compressor maintained the circulation of gases required to fluidize the bed of sand and to convey coal from the feeder. As a run progressed the pyrolysis gas constituted an increasing percentage of the total system gas as it replaced the original nitrogen gas in the system.

Approximately 1L of pyrolysis gas was collected in a sealed polyethylene bag at the end of a run. Analysis of the gas sample for CO, CO_2, H_2, C1 to C4 hydrocarbons, BTX, and water was performed using two gas chromatographs. The instruments and procedures for this analysis are summarized in Table 3.1. The product gas composition was calculated on a N_2-free basis. Knowing the volume and composition of the gas collected and the

Table 3.1. Conditions of GC analysis for gaseous products

Data station : Perkin-Elmer Sigma 10B

Instrument 1 : Perkin-Elmer Sigma 4B

Detector	TCD
Carrier gas	He
Gas flow rate	25ml/min
Sample size	0.25ml

Column A : MS-5A (80/100 mesh), 6ft X 0.125in.o.d.

Compounds analyzed	CO, H_2
Temperature	60°C

Column B : Poropak Q (80/100 mesh), 8ft X 0.125in.o.d.

Compound analyzed	CO_2
Temperature	60°C

Instrument 2 : Perkin-Elmer Sigma 3B

Detector	FID at 195°C
Injection temp.	195°C
Temp. program	55°C for 4min 55-195°C, gradient 8°C/min 195°C for 10min

Column A : Poropak Q (80/100 mesh), 8ft X 0.125in.o.d.

Compounds analyzed	C_1-C_4 hydrocarbons
Carrier gas	N_2 at 3ml/min
Sample size	0.25ml

Column B : DB-5 (1.5micron coating), 30m X 0.5mm o.d.

Compounds analyzed	Benzene, Toluene, Xylene
Carrier gas	N_2 at 8ml/min
Sample size	0.50ml

coal feed rate, the percent conversion of the coal to the gaseous components can be calculated.

Although the gas concentration of pyrolysis products was increasing during a run, the gas composition expressed on a N_2-free basis was constant. Since the gas meter provided the volume of pyrolysis gas produced, the percent conversion to gaseous products could be calculated.

Eight 1L plastic bottles collected mostly water and water soluble products from the two condensers. The water content of this fraction was determined by Karl-Fischer titration. The cotton wool filter was weighed to determine the quantity of tar collected and the cotton wool was discarded. Products collected in the Schrader bellows separators were weighed and stored. The remaining tar was washed from the condenser piping with tetrahydrofuran (THF) from J.T.Baker Chemical Company. The wash solution was filtered to remove char and its water content was determined by Karl-Fischer titration. The solvent was then evaporated at 65°C and 20-inch Hg vacuum and the tar residue was weighed and stored in a refrigerator. The recovered THF was analyzed for water content by Karl-Fischer titration and then reused in the following runs. Usually water in the wash solution was almost quantitatively evaporated with THF and therefore the remaining tar was almost free of water.

Char production was determined from the weight of char in the char pot and from the quantity of char filtered from the solvent washings. Char was removed from the Char pot and stored for analysis. Knowing the weight of coal fed and the quantities of char, tar, water and gas produced, material balances were calculated.

Ultimate analyses of the char and tar products were performed using the Perkin-Elmer Model 240 elemental analyzer. These data combined with the gas analysis and coal feed ultimate analysis allowed the calculation of elemental balances for C, H, N,and O. An ash balance for every run was assumed to be 100 % because of the difficulty in obtaining a representative sample of char which was accurate enough to allow calculation of a balance.

BENCH SCALE PYROLYSIS

The bench scale pyrolysis unit is shown in Figure 3.2 and details of the reactor in Figure 3.3.

The standard apparatus consists of a mechanically stirred entrained flow feeder, a fluidized bed reactor, a cyclone, condensers, filters and a gas collection bag. Details of the feeder operation are described elsewhere by Scott and Piskorz (3). Two identical fluidized bed reactors were used in this investigation both having net volumes of 154.55 ml. One was constructed of Inconel and the other of Type 304 stainless steel.

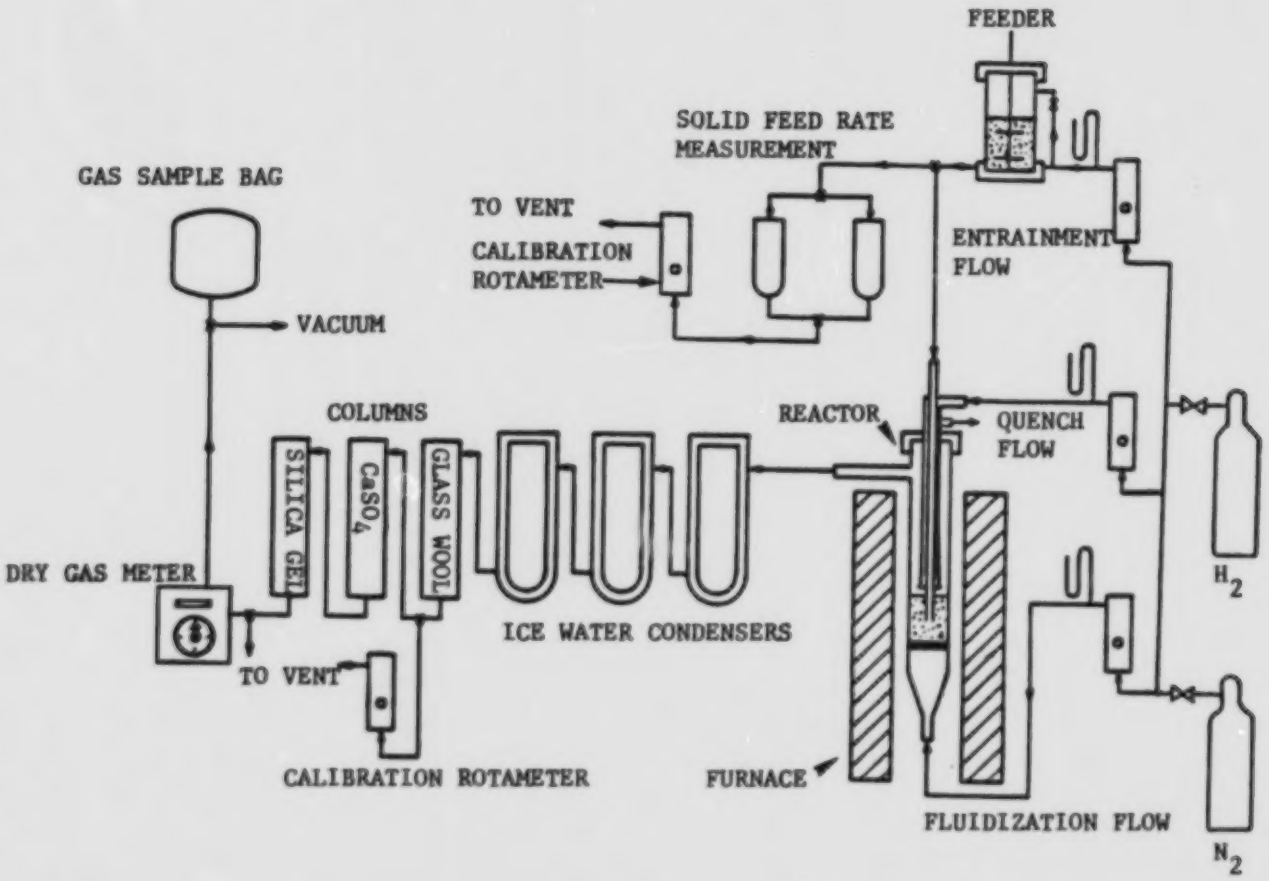


Fig.3.2. Bench scale flash pyrolysis unit.

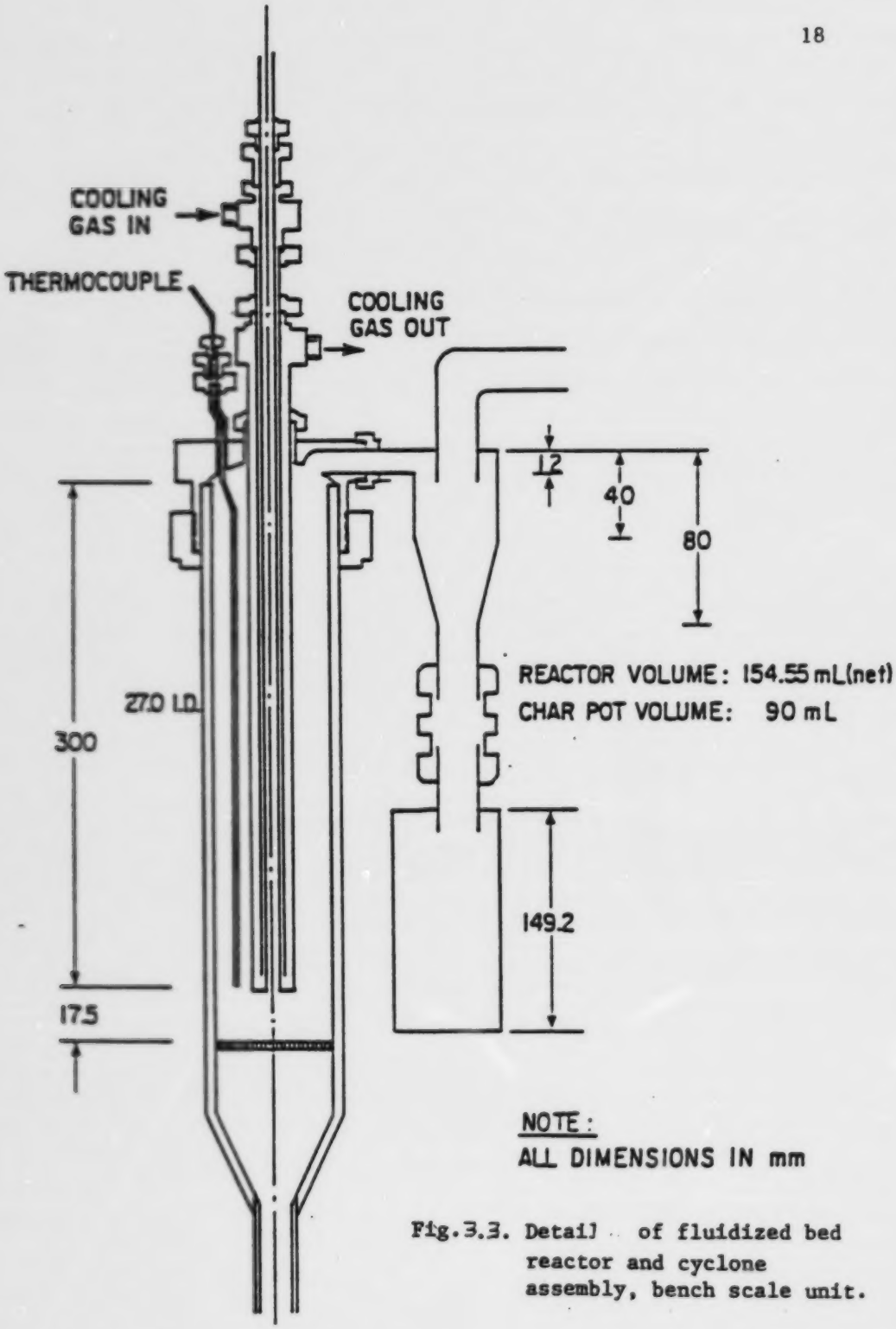


Fig.3.3. Detail of fluidized bed reactor and cyclone assembly, bench scale unit.

Coal or other feed particles were fed to the reactor entrained in a stream of N_2 or H_2. The reactor injection tube could be air cooled to prevent plugging when coprocessing residues or caking coals were fed.

The bed consisted of Ottawa testing sand typically screened to -590 + 300 μm (-30 + 50 mesh).

A second stream of N_2 or H_2 provided the fluidizing gas for the bed. Vapour residence times could be varied by adjusting the volume of sand in the bed and/or the fluidizing plus feeder gas rate. The reactor-cyclone-char pot assembly was inside the furnace permitting the pyrolysis reaction and product separation to occur at the same temperature. This prevented the hot vapours from condensing in the char pot. Gas and tar vapours were collected in a split stream system consisting of four ice-water condensers, two cotton wool filters and a polyethylene gas bag. Condensible liquid products either condensed on the walls of the glass condensers or formed a fog that was removed by the cotton wool filters. The remaining gaseous product was collected in a sealed polyethylene bag with an approximate volume of 170 L. The total volume of gas collected during a run was measured by a dry gas meter. The absorption tubes for water and light hydrocarbons were optional and were not normally used in the studies of coal pyrolysis or pyrolysis of coprocessing residues.

Analysis of the gas sample for CO, CO_2, C_1 to C_4 hydrocarbons and BTX was performed using two gas chromatographs. The instruments and procedures for this analysis are the same as those given previously for the pilot plant pyrolysis experiments.

Conditions of GC analysis for CO, CO_2 and C_1 to C_4 hydrocarbons were previously summarized in Table 3.1. Conditions of GC analysis for gaseous BTX were also shown in Table 3.1.

Two 15 ml sample vials connected beneath the first two condensers were used to collect water and water soluble oils. The water content of this liquor was determined by Karl-Fischer titration. The quantity of tar stopped by the cotton wool filter was determined by weighing the filters before and after the run. The remaining tar was washed from the condenser walls and tubing with tetrahydrofuran (THF). The washings were filtered to remove any char and the water content of the solution was determined by Karl-Fischer titration. This THF solution was analyzed for major organic compounds contained in the tar, using high resolution gas chromatography. Conditions of GC analysis are described in Table 3.2. The solvent was then evaporated at about 65°C under 20 inches Hg vacuum.

The reactor-cyclone-char pot assembly was weighed before and after each run to determine the quantity of char collected in the char pot and in the bed. The char filtered from the solvent

Table 3.2. Conditions of gas chromatographic separation

Data station	Perkin-Elmer Sigma 10B
Instrument	Perkin-Elmer Sigma 3B
Column	DB-5, 30m x 0.5mm o.d.
Detector*	FID at 290°C
Injection temp.	290°C
Carrier gas	N2 at 8ml/min
Temp. programme	
	65°C for 3min
	65-290°C, gradient 5°C/min
	290°C for 2min
Sample	THF or Toluene soluble fraction(in toluene) 0.3μl

Note: * The response factor for each component is assumed to be 1.0, because the influence of the factor on the results seems to be insignificant in the present study.

washings was dried and weighed and included in the char determination.

Material balances were calculated knowing the weight of coal fed and the quantities of char, tar, water and gas collected.

RESULTS AND DISCUSSION

Part A

4. PYROLYSIS OF LOW RANK COALS

4.1 INTRODUCTION

As mentioned in Chapter 1, the fluidized bed reactor appears to be very suitable device for the pyrolysis of lignites or subbituminous coals. No operating problems were encountered in the bench scale unit and product yields were about the same as those obtained by others.

On the basis of the previous findings on the bench scale unit, liquid yields from Saskatchewan (Coronach) lignite and Alberta (Forestburg) subbituminous coal were evaluated as a function of process conditions on the larger scale than the previous work, in the 1-3kg/h flash pyrolysis unit.

The coals used in this study include three samples of Coronach lignite and a Paintearth seam lot of Forestburg subbituminous coal as listed below. All lignite samples were supplied by the Energy Research Laboratories of CANMET, and the Forestburg coal was supplied by Luscar Ltd. of Edmonton, Alberta.

1. Coronach lignite #1, received in January, 1985.
2. Coronach lignite #2, received in October, 1985.
3. Coronach lignite #3, received in January, 1986.
4. Forestburg subbituminous coal, received in January, 1986.

4.2 MATERIALS

4.2.1 PREPARATION OF CORONACH LIGNITE

Approximately 30 kg of Coronach lignite #2 in water slurry form was received from the Ontario Research Foundation. About 15kg of the sample was dried under nitrogen at 55°C for 2 days. Following drying, the lignite was passed through a sample grinder to break up the agglomerated chunks of dry coal particles. The grinder (Sturtevant Mill Co.) was adjusted to minimize size reduction of the individual particles. A particle size analysis was performed using a Ro-Tap Testing Sieve Shaker (C.E. Tyler Industrial Products).

Another 15 kg of the sample was dried under air at 105°C for 24 hours to obtain a sample of lower moisture content than the previous one. Hopefully, good material balances and good analytical results can be attained if dry feeds are used. On the other hand, it might be anticipated that coal drying can affect physical structure and thus influence the pyrolysis behaviour of coal.

This lot of coal was designated as Coronach lignite #2 to distinguish it from a previous sample from the same deposit.

Coronach lignite #3 was received in a pulverized powder form and utilized as received. When this sample was received, it contained about 30% moisture. During the storage at room temperature, the moisture content was brought to approximate equilibrium

with the laboratory atmosphere. Therefore, the moisture gain or loss could be made minimal during sampling operations. This sample was also subjected to an acid washing treatment in order to determine the significance of the inorganic fraction. Details of the acid washing treament are discussed in a later section.

4.2.2. PREPARATION OF FORESTBURG SUBBITUMINOUS COAL

A Paintearth seam lot of Forestburg subbituminous coal was received from Luscar Ltd., Edmonton, Alberta. The top size of the Paintearth seam lot had been reduced to between 1to 3 inches due to primary breaking, which would take place at the mine. This lot was kept at room temperature in a barrel and during the storage the moisture content of each lump of coal was brought to approximate equilibrium with the laboratory atmosphere.

About 10kg of the sample was subjected to pulverization by the same sample grinder as used for Coronach lignite #2. The grinder used is a disk attrition type mill and the top size of each lump of coal had to be reduced to the 0.5 inch range so as to pass through the inlet nozzle of the grinder. Following this preparative crushing, the coal was fed to the grinder. Size reduction was accomplished in three successive grinding operations, during which the space between the attrition disks was gradually narrowed using the controller and finally this space was adjusted to produce coal particles comminuted to pass through a 250μm (60 mesh) sieve.

The pulverized coal was kept in a plastic receptacle in order to minimize the gain or loss of moisture before feeding to the pyrolysis reactor.

4.2.3. COAL CHARACTERIZATION

All the coals were characterized by ultimate and proximate analysis. CHN analysis of the coals was done using a Perkin-Elmer Model 240C elemental analyzer. This micro-analytical technique required a few mg sample of coal dried in an oven with air circulation at 105°C for about 24 h.

To obtain a representative ash content three samples of about 1 g of coal were heated and burned in an adequately ventilated muffle furnace at 950°C for 2 h.

Moisture was determined by drying three 1 g samples in air at 105°C for about 24 h.

Proximate analysis of the coals was done using micro computer controlled thermogravimetry (Perkin-Elmer Model TGS-2). This method is reported to provide a rapid determination of moisture, total volatiles, fixed carbon, and ash content of coal which agree with results from more time consuming standard ASTM methods (7). Because of the small sample size it was decided that moisture and ash contents were best determined from the larger 1 g samples as described above (8).

Tables 4.1 and 4.2 give ultimate and proximate analyses of the samples of Coronach lignite and Forestburg subbituminous coal (Paintearth seam), as well as the analyses for Estevan lignite #4 and Forestburg #2, both of which were used in previous experiments to determine the effect of acid washing on pyrolysis behaviour (9). In addition, analyses of Forestburg subbituminous coal (Paintearth seam lot) given by Luscar Ltd. are listed for comparison.

The proximate analyses were corrected according to the procedure shown in Table 4.3, because TGA ash and moisture determinations could have a large inherent error due to the very small sample size used.

The results illustrate the difficulty in obtaining comparison of data among different laboratories because of the variability in the composition of the coal samples used. Even in samples of the same deposit, for example, within the Coronach lignite samples, there seems to exist a significant difference in the elemental composition and the ash content of the coal samples. Similarly, a very large difference in oxygen content of Forestburg subbituminous coal (Paintearth seam lot) is obvious between data from the two laboratories. This appears to reflect the existence of a state of heterogeneity between samples originating in the same seam.

Table 4.1 Ultimate analysis of coal samples

	wt %				
	C	H	N	O (by diff.)	H/C (atomic ratio)
Coronach lignite					
#1	55.56	4.40	0.81	39.23	0.95
#2	67.65	4.34	1.25	26.76	0.77
#3	66.54	4.38	0.83	28.25	0.79
acid washed#3	63.80	4.07	0.76	31.37	0.77
Forestburg subbituminous coal (Paintearth seam)					
Waterloo	67.65	4.43	1.77	26.15	0.79
Luscar (Diplomat seam)	73.58	5.63	1.42	19.37	0.92
#2*	69.85	3.65	1.88	24.62	0.63
Estevan lignite					
#4*	67.58	4.26	1.17	26.99	0.76

Note: * Data from Scott,1986.

Table 4.2 Proximate analysis of coal samples

	Moisture (oven-drying)	Volatiles	Fixed carbon	Ash (muffle furnace)	Ash(dry)
	wt % as is basis				wt%
Coronach lignite					
#1	12.01	37.42	34.73	15.84	18.00
high moisture #2	9.59	38.39	41.70	10.32	11.42
low moisture #2	2.77	41.28	44.87	11.10	11.42
#3	22.77	32.50	32.21	12.52	16.21
acid washed #3	20.91	33.16	38.95	6.98	8.83
Forestburg subbituminous coal (Paintearth seam)					
Waterloo	19.05	29.59	44.40	6.96	8.60
Luscar	26.00	27.87	34.12	12.09	16.34
(Diplomat seam)					
#2*	11.06	38.45	44.87	5.62	6.32
Estevan lignite					
#4*	6.68	41.66	45.41	6.25	6.70
	wt % maf				
Coronach lignite					
#1	---	51.86	47.97	---	---
#2	---	47.93	52.09	---	---
#3	---	50.22	49.78	---	---
acid washed #3	---	45.99	54.01	---	---
Forestburg subbit. (Paintearth seam)	---	39.99	60.01	---	---

Note: * Data from Scott,1986.

Table 4.3

Correction for proximate analysis
(sample calculation)

Example: Forestburg subbituminous coal

(1) Data

Moisture(oven-drying)	19.05 wt%	'as is' basis
Ash(muffle furnace)	6.96 wt%	'as is' basis
Thermogravimetric analysis(TGA)		
Moisture	18.74 wt%	
Volatiles	29.70 wt%	
Fixed carbon + Ash	51.56 wt%	

(2) Data correction

Volatiles = 29.70(1-0.1905)/(1-0.1874) = 29.59 wt%

Fixed carbon + Ash = 51.56(1-0.1905)/(1-0.1874)

= 51.36 wt%

Fixed carbon = 51.36 - 6.96 = 44.40 wt%

The volatile matter content of Forestburg subbituminous coal is about 10% less than that of Coronach lignite (39.99% vs. 47.93-51.86%) on the basis of moisture-ash-free coal.

Thermogravimetric measurements of these coals are shown in Figures 4.1, 4.2, 4.3 and 4.4. The progress of decomposition is followed by recording weight losses that accompany coal pyrolysis. These measurements indicate that the weight loss for Coronach lignite #3 begins slightly earlier than that for Forestburg subbituminous coal and that there is little difference between the original and acid washed Coronach lignite #3.

As regards volatile matter, however, it has been pointed out by many researchers that the analytically determined volatile matter content does not necessarily correlate with the yield of volatile products in fast pyrolysis studies using the grid heating pyrolyzers (10)(11) and the fluidized bed pyrolyzers, especially for low rank coals (1)(5).

The discrepancies between the coal volatiles determined by proximate analysis and observed by fast pyrolysis could be ascribed in general to the influence of parameters, which are related to the transport of the volatile species from the interior to the surfaces of the coal. Thus, the degree of devolatilization in coal pyrolysis could be strongly dependent on the heating rates and the maximum temperature at which the volatile species were generated through thermal decomposition.

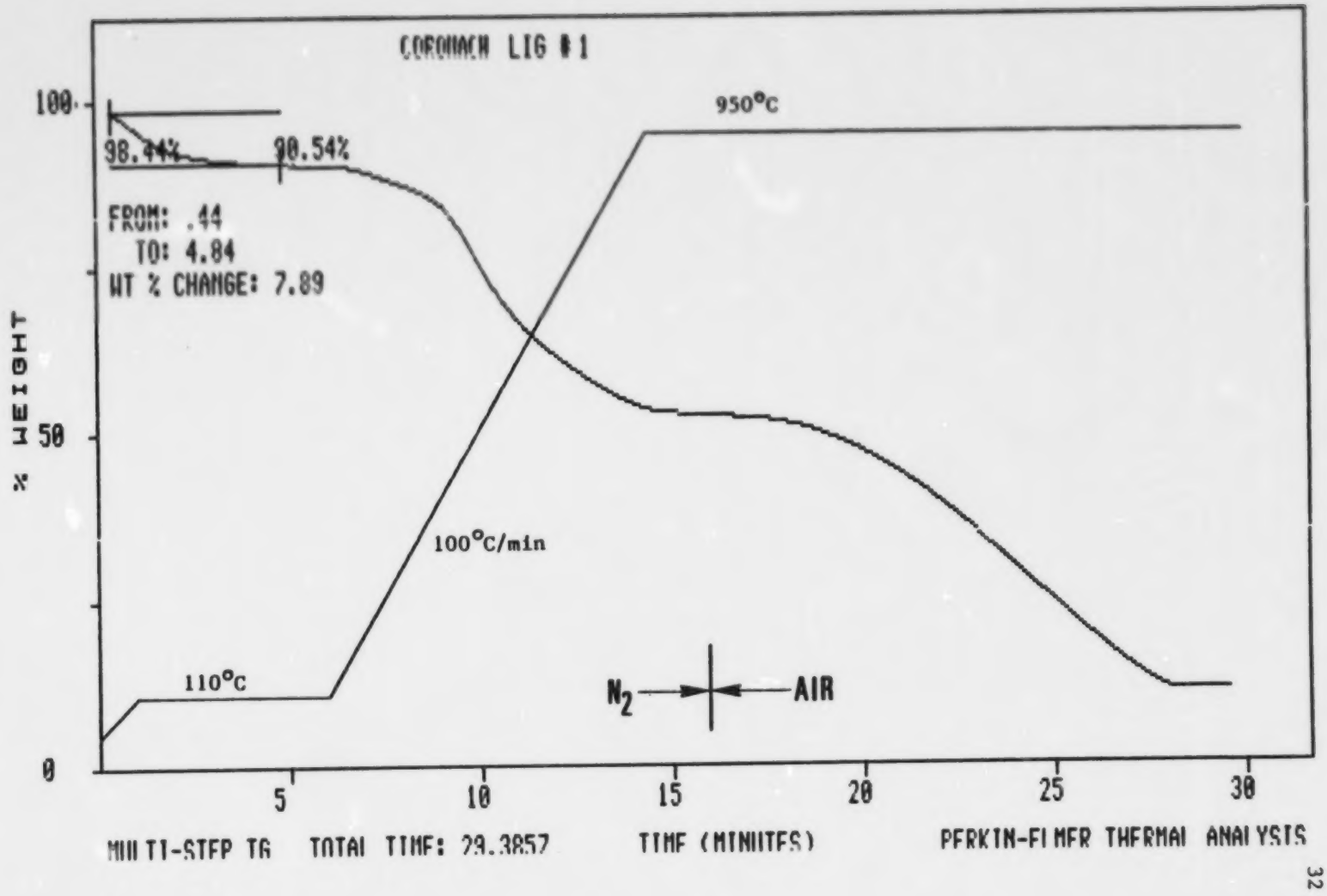


Fig. 4.1 Thermogram of Coronach lignite #1 in N_2.

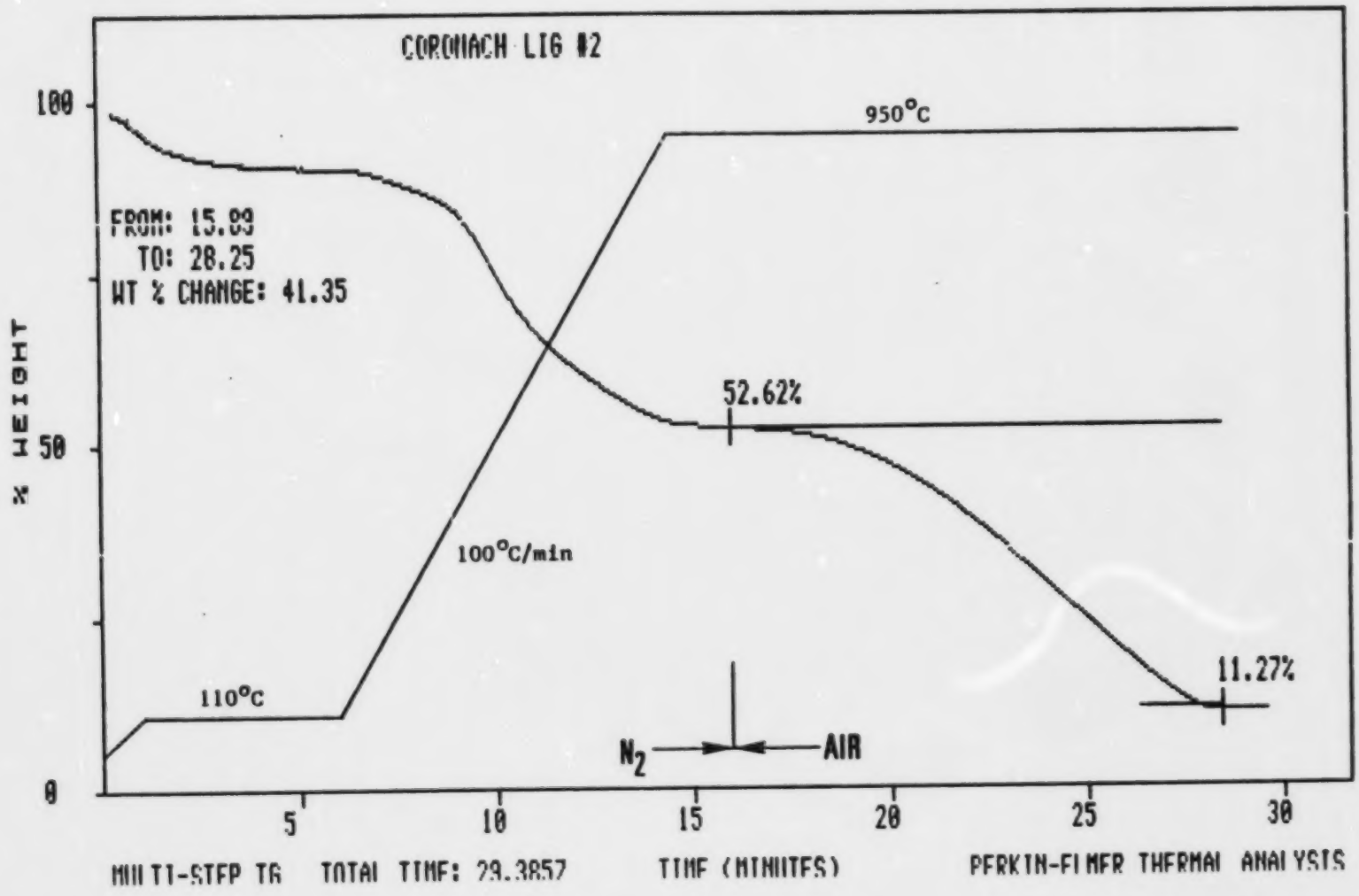


Fig. 4.2 Thermogram of Coronach lignite #2 in N_2.

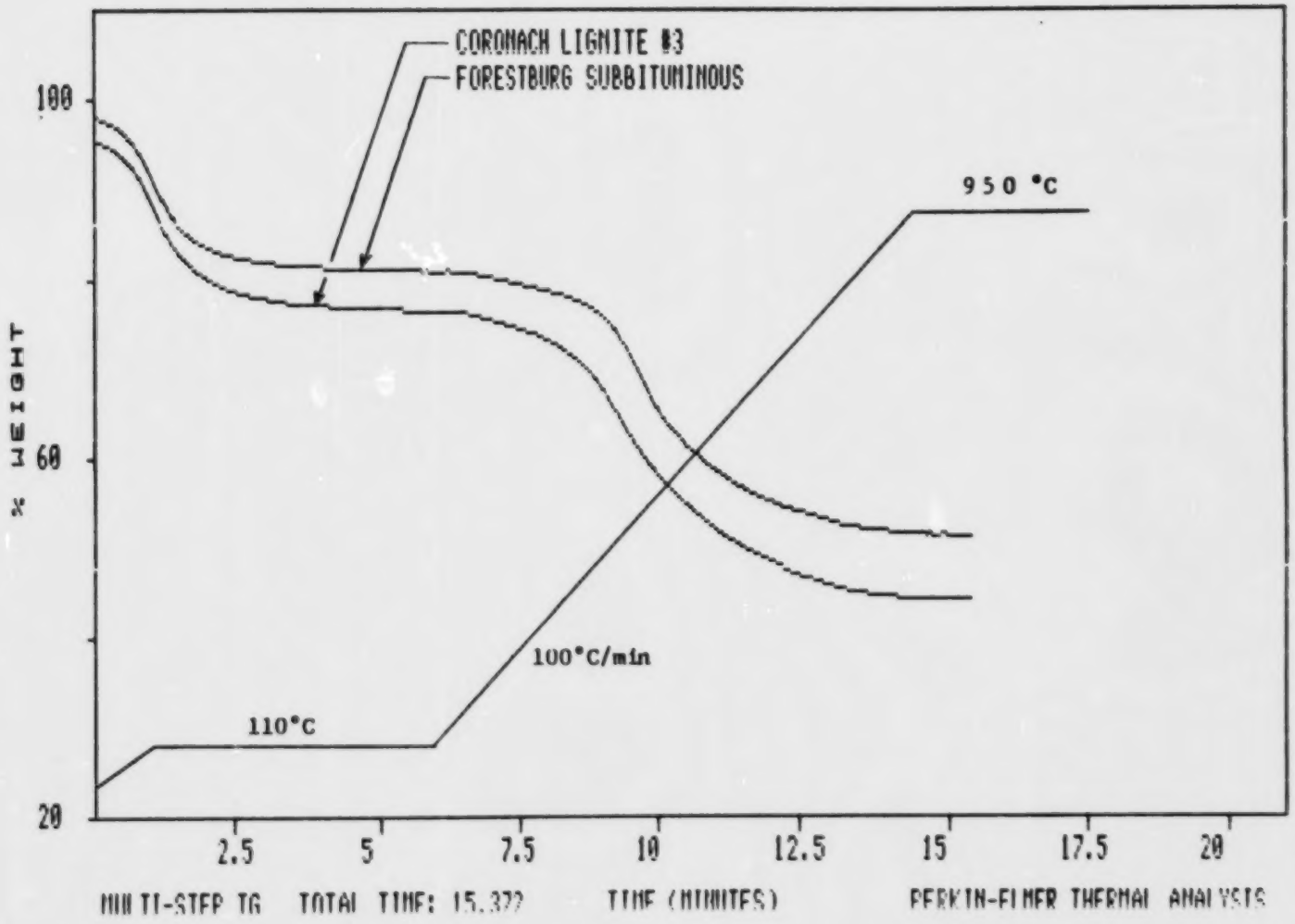


Fig. 4.3 Thermogram of Coronach lignite #3 and Forestburg subbituminous coal in N_2.

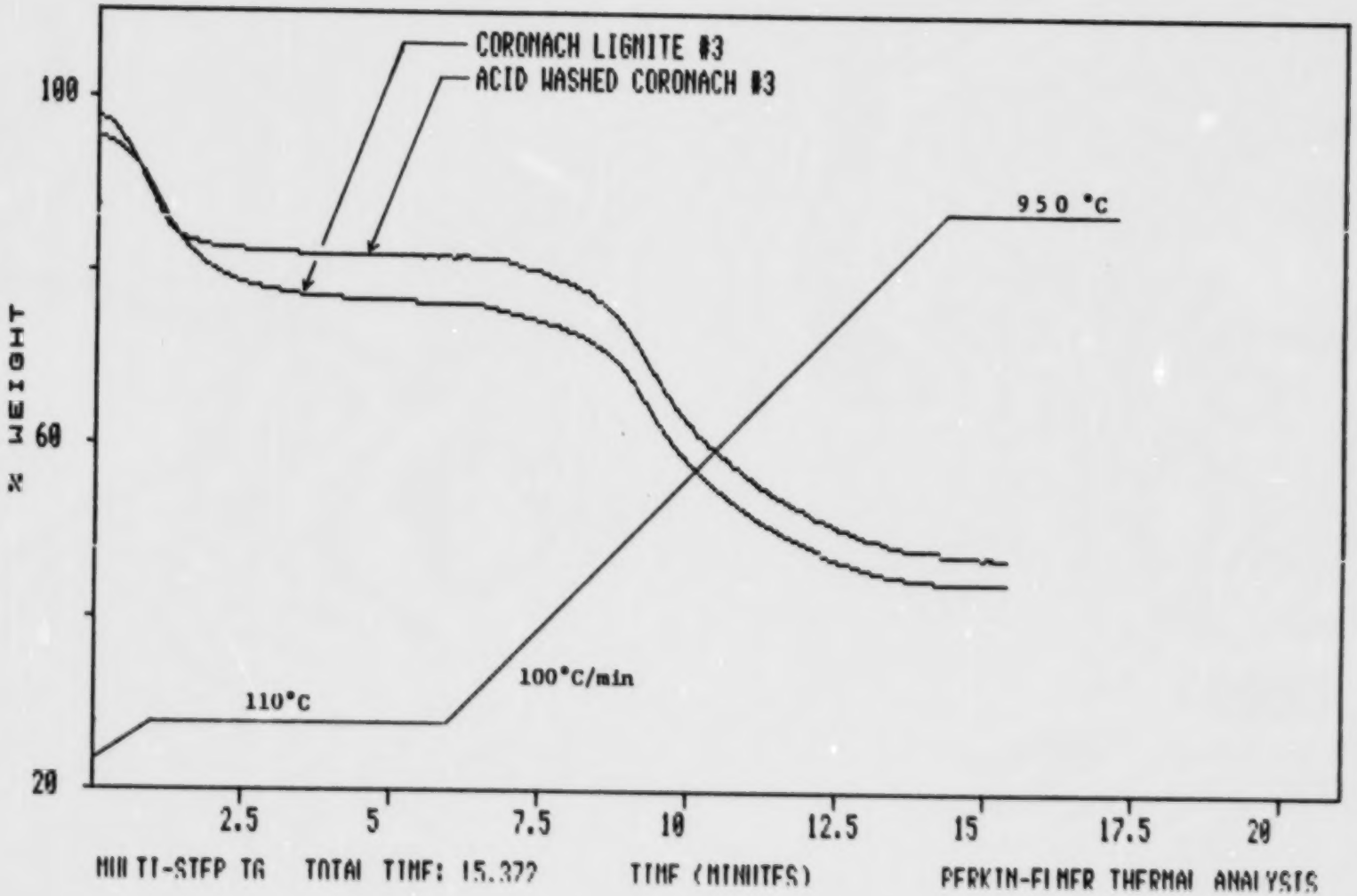


Fig. 4.4 Thermogram of acid washed Coronach lignite #3 in N_2.

Table 4.4 gives the particle size distribution of the pulverized coal samples. Coronach lignite #1 is included in the table to allow the particle size distribution of the previously prepared coal to be compared with that currently employed in the present pilot plant pyrolysis. From Table 4.4 it is indicated that very small amounts, except for Coronach lignite #1, are larger than 590μm, namely 0.51% in Coronach lignite #2 and 0.04% in Forestburg subbituminous coal. These small fractions consisted of easily broken agglomerated particles. A significant fraction of the samples was smaller than 149μm. These small particles were present in the "as received" sample in the case of Coronach lignite #3. On the other hand, they were produced concomitantly during grinding of each lump of coal in the case of Forestburg subbituminous coal. All the coal samples, except for Coronach lignite #1, have very similar particle size distribution. The smaller -74μm particles were reported to give lower tar and gas yields with both Saskatchewan (Estevan) lignite and Forestburg subbituminous coal (5). Therefore, it is of great importance to treat particle size variation as one of the basic variables for optimal pyrolysis. Judging from this point of view, it is most desirable that the particles smaller than 74μm should be minimized in the size reduction process if the maximum tar yield is to be attained.

Table 4.4 Particle size distribution of coal samples

Mesh	+28	-28 +60	-60 +100	-100 +200	-200	total
Micrometer	+590	-590 +250	-250 +149	-149 +74	-74	
Coronach lignite	wt %					
#1	23.70	35.60	10.91	11.02	18.33	99.56
high moisture#2	0.51	36.88	29.14	20.82	12.65	100.00
low moisture #2	0.00	42.93	29.02	18.27	9.78	100.00
#3	0.00	48.31	34.47	11.49	5.73	100.00
Forestburg subbituminous coal (Paintearth seam)	0.04	40.68	31.47	19.53	8.23	100.00

As seen in Table 4.4, those small particles range between 5.73% and 18.33% and these contents seem to be an acceptable level considering the fact that it is extremely difficult to determine exactly the degree of size reduction that can be achieved in the comminution device.

4.3 PRELIMINARY EXPERIMENTS

The pilot plant experiments were numbered as P-(number) to distinguish them from experiments using the bench scale reactor.

A preliminary experiment was performed using Waterloo flash pyrolysis process (pilot plant unit) to compare the results with those obtained from Coronach lignite #1 using the bench scale unit (see Figures 6.1 and 6.2).

The results are shown in Table 4.5.

The particle size distribution of Coronach lignite #1 was given in Table 4.4. The coal size range for the bench scale run was -250 +74 μm , whereas the coal size for the pilot plant run included everything less than 3175 micrometer (-8 mesh).

From results shown in Table 4.5, it is indicated that the pilot plant run produced more char and tar and less gas than a similar run using the bench scale unit. The yields of pyrolytic water showed good agreement. Possibly some sand was blown out of the reactor and into the char pot resulting in the higher char

Table 4.5. Product yields of bench scale unit and pilot plant unit, pyrolysis of Coronach lignite #1.

Run No.	178	P-55
Feed	Bench Unit N_2 atm	Pilot Plant N_2 + recirculated gas
Temperature, °C	590	585
Coal Size, μm	-250 +74	-3175
Sand Size, μm	-590+300	-840+590
Sand Amount, gms	60	2100
Duration of Run, min.	35.0	187
Wt. of Coal Fed, gms	47.39	4505.5
Vapour Residence Time, secs.	0.55	0.54
Moisture in Feed, wt. %	12.01	12.01
Ash in Feed, dry wt. %	20.46	20.46
Yields, wt. % maf		
Gas	20.55	14.47
Tar	11.06	14.65
Char	57.56	69.00
Water	11.02	9.97
Total Recovery	100.19	108.09
Yields of Gases, wt. % maf		
H_2	1.58	0.07
CO	3.74	4.06
CO_2	11.43	8.70
CH_4	1.61	1.33
C_2H_4	0.24	0.10
C_2H_6	0.18	0.12
C_3	1.40	0.06
C_4	0.37	0.04
BTX	N.D.	N.D.

Note: N.D. - Not Determined

yield and total recovery. It is also possible that the bench scale unit produces less char and more gas than the pilot plant because the char is kept at the run temperature for the duration of the run. As described previously, the pilot plant char pot is neither heated nor insulated and therefore the separated char quickly cools well below the run temperature.

The ultimate analysis of pyrolysis products is given in Table 4.6, together with the elemental balance for each pyrolysis run. Results shown in Table 3.6 indicate that pilot plant chars have higher hydrogen, nitrogen and oxygen contents than bench scale char. This suggests that bench scale char has undergone greater devolatilization than pilot plant chars and has therefore yielded more gaseous products. Contrary to gas yields, however, tar yields were higher for pilot plant runs than for bench scale runs. Presumably the slow char devolatilization in the hot char pot preferentially yields gaseous products as opposed to liquid products. These observations parallel those for increasing vapour residence times as reported by Scott (5). It was reported that increasing the vapour residence time reduced char and tar yields while increasing the gas yields. It is possible that a hot cyclone and char pot will affect the pyrolysis reactions in the same way that a longer vapour residence time does.

Table 4.5 also shows that the H_2 and C_3 gas yields for the bench scale run are higher than would be predicted by previous results for Estevan lignite pyrolyzed at 650°C or by results

Table 4.6. Ultimate analysis and elemental balance of pyrolysis products, Coronach lignite #1.

		Run 178 Bench Scale Unit	Run P55 Pilot Plant Unit	
Feed as is, (maf)	C	48.89 (55.56)	48.89 (55.56)	
	H	3.87 (4.40)	3.87 (4.40)	
	N	0.71 (0.81)	0.71 (0.81)	
	O	(39.23)	(39.23)	
	Ash	15.84 (20.46) dry	15.84 (20.46) dry	
	H_2O	12.01	12.01	
	H/C	0.95	0.95	
Tar	C	74.59	42.01	66.69
	H	7.07	9.26 from	7.00 Washed
	N	1.20	1.17 Schroder	1.42 from
	O	17.14	47.56 Bellows	24.89 Condensers
	H/C	1.14	2.65	1.26
Char as is, (maf)	C	69.75 (89.32)	53.25 (72.42)	54.42 (80.23)
	H	1.86 (2.38)	2.41 (3.28) from	1.89 (2.79) from
	N	0.48 (0.61)	0.77 (1.05) filter	0.53 (0.78) char
	O	(7.69)	(23.25) paper	(16.20) pot
	Ash	21.91 [27.61]	26.47 [24.14]	32.17
	H/C	0.32	0.54	0.42
Gas	C	37.98	37.09	
	H	11.24	3.12	
	O	50.78	59.79	
C Balance		98.92	93.7	
H Balance		153.33	102.1	
O Balance		65.92	80.9	
Ash Balance		79.33 [100]	133.3 [100]	

Note: Values in square brackets have been adjusted for 100% asn balance.

reported by Scott (5) at 600°C. On the other hand, pilot plant yields of H_2, C_3 and C_4 gases are usually low. It is possible that the larger particle sizes fed to the pilot plant introduced some mass and/or heat transfer limitations which hindered the release of specific product species. Also, recirculation of product gases could affect individual product yields, especially if there is a source of hydrogen.

The operation of the pilot plant with a lignite feed was not difficult. The run continued until the feed supply in the hopper was exhausted. The feed rate was 1.45 kg/h and was kept as low as possible to maintain the temperature above 580°C. Feeding the coal did not present any problems and the pressure drop across the reactor remained constant which suggested that char accumulation in the fluid bed was minimal. A potential problem area was indicated by an increasing pressure drop across the cold condenser. The hot condenser temperature was lowered from 60°C to 20°C in order to condense more tar in this condenser and thus reduce the plugging of the second ice-water condenser. The condenser tubes were washed with a mixture of methanol, methylene chloride, and tetrahydrofuran and the solvent was evaporated to recover about 46% of the tar product. Another 22 percent of the tar was recovered in the separators. The remainder was collected in the cotton-wool filter and condensate bottles.

4.4 EFFECT OF THF ADDITION

Two pilot plant runs, P-70 and P-71, were performed with Coronach lignite #2. In an effort to minimize plugging of the product collection system, i.e., condensers, tubing and filter, tetrahydrofuran (THF) was injected into the top of the reactor at 4.9ml/min during Run P-70. THF is an excellent solvent for the liquid products of coal pyrolysis. It was hoped that the THF vapour, formed in the top of the reactor, would mix with the organic liquid vapours and upon condensation help to carry the condensed products into the collection bottles attached to the condenser tubes. However, it is suspected that the THF decomposed at the high temperatures up to about 650°C present at the top of the reactor. This decomposition is evidenced by the high yield of light gases as shown in Table 4.7. Less than 10% (52.7 g) of the total THF injected (537.97 g) was collected in the condensate fraction. The remainder of the THF and its decomposition products were probably collected in the cotton wool filter and in the gas product. The THF-free yields for Run P-70, given in Table 4.7, were calculated by assuming that the remaining 90% (485.6g) of the THF was collected in the gas fraction. During Run P-70, the cotton wool filter collected 3.8% more products (on maf coal fed basis) than it did during Run P-71 without THF injection. Run P-71 also had an additional Schrader bellows condensate trap located between the second condenser and the cotton wool filter. This trap collected 11g of liquor and 20g of tar. If no trap had

Table 4.7. Pyrolysis of Coronach lignite #2, effect of THF addition.

Run No. Feed	P-65 Coronach #1 Pilot Plant	P-70 Coronach #2 Pilot Plant THF Addition	P-71 Coronach #2 Pilot Plant
Temperature, °C	647	646	651
Coal Size, μm	-1680	-590	-590
Sand Size, μm	-840 +590	-840 +590	-840 +590
Sand Amount, gms	2100	2100	2100
Duration of Run, min.	133	124	115
Wt. of Coal Fed, gms	3005.1	3088.2+537.97 THF	2962.9
Vapour Residence Time, secs.	0.50	0.5	0.5
Moisture in Feed, wt. %	10.86	9.59	9.59
Ash in Feed, dry wt. %	18.68	11.42	11.42
Yields, wt. % maf		THF Free	
Gas	16.77	(8.19) 23.70	17.12
Tar	11.37	(18.22) 17.31	15.10
Char	60.63	(61.81) 50.72	60.93
Water	10.95	(13.90) 10.05	11.05
Total Recovery	99.72	(102.12) 101.78	104.20
Yields of Gases, wt. % maf			
H_2	0.15	0.19	0.11
CO	6.70	10.90	7.86
CO_2	7.84	9.25	6.91
CH_4	1.70	3.46	1.76
C_2H_4	0.15	2.44	0.28
C_2H_6	0.11	0.75	0.10
C_3	0.06	0.70	0.05
C_4	0.06	0.46	0.05

been present, the liquor, which was mostly water, would have been collected in the cotton wool filter and weighed as tar. This would result in the tar yield for Run P-70 being overestimated. Operating conditions were identical in Runs P-70 and P-71 other than the THF injection for Run P-70. The THF and its decomposition products are probably distributed between the gas and the cotton wool filter.

It is also possible that the decomposition products of THF took part in secondary reactions with coal pyrolysis products and thus affected the product distribution. The THF injection would also have had a quenching effect on the coal pyrolysis products reducing the influence of secondary reactions. Because of these questions, the duplicate run P-71 was performed to eliminate the effect of THF.

4.5 COMPARISON OF CORONACH LIGNITES

A comparison can be drawn between the yields of the two Coronach lignite samples (Runs P-65 and P-71) from the results given in Table 4.7. The high mass balance of Run P-71 may weaken somewhat the validity of the comparison. It is likely that char and water yields are overestimated in this run resulting in the high recovery. Sand from the bed may have been carried over into the char pot resulting in an overestimated char fraction. The THF used to dissolve the tar in the condensers contained an unknown quantity of water which was later collected and designated as a

coal pyrolysis product. It could be concluded, however, that the gas yields from the two lignites are almost identical (16.77% vs. 17.12% maf) while Coronach #2 has a higher tar yield compared to Coronach #1 (15.10% vs. 11.37% maf).

Although the total gas yields are very similar, the yields of carbon oxides differ slightly. The yields of CO and CO_2 for Run P-71 were 7.86% and 6.91%, respectively. For Run P-65, these yields were 6.70% and 7.84%. The ash content of a dry Coronach #1 sample was 18.68% while that of a dry Coronach #2 sample was only 11.42%.

Table 4.8 gives the ultimate analysis and elemental balances of pyrolysis products for Runs P-65 and P-70. Analyses and balances for Run P-70 include the injected THF and its products. However, the coal feed, tar and char analyses should be unaffected by the THF. This will not be true, of course, if the THF is involved in secondary reactions with tar and char products. Coronach #2 has a much higher carbon content (67.65% vs. 55.56% maf) and lower oxygen content (26.76% vs. 39.23% maf) than Coronach #1 as shown in Table 4.2. The hydrogen and nitrogen contents are similar. Coronach #2 has a correspondingly lower H/C atomic ratio than Coronach #1 (0.77 vs. 0.95). Tar produced from Coronach #2 has a slightly higher hydrogen content (8.26% vs. 7.32%) and a higher H/C atomic ratio (1.36 vs. 1.19) than tar produced from Coronach #1. The char from Coronach #2 has a

Table 4.8. Ultimate analysis and elemental balance of pyrolysis products from Coronach lignite #1and #2.

Run No.		P-65 Coronach #1	P-70 Coronach #2 THF Injection
Feed as is, (maf)	C	48.89 (55.56)	54.18 (67.65)
	H	3.87 (4.40)	4.54 (4.34)
	N	0.71 (0.81)	1.00 (1.25)
	O (diff)	(39.23)	(26.76)
	Ash	15.84 (18.00)	10.32 (11.42)
	H_2O	12.01	9.59
	H/C	0.95	0.77
Tar	C	73.54	72.88
	H	7.32	8.26
	N	1.09	1.61
	O (diff)	18.05	17.25
	H/C	1.19	1.36
Cnar as is, (maf)	C	57.59 (73.80)	72.41 (88.35)
	H	1.91 (2.45)	2.61 (3.18)
	N	0.80 (1.03)	0.97 (1.18)
	O (diff)	(22.72)	(7.29)
	Asn	21.96	18.04
	H/C	0.40	0.43
Gas	C	39.40	47.31
	H	3.78	6.21
	O	56.82	46.48
	H/C	1.15	1.58
C Balance		118.66	98.04
H Balance		101.42	113.21
O Balance		92.10	101.40
Asn Balance		79.93	104.56

Notes: 1. THF: C_4H_8O, C 66.63%, H 11.18%, O 22.19%

2. ( ): moisture free values

higher carbon content (88.35% vs. 73.80% maf) and a slightly higher hydrogen content (3.18% vs. 2.45%) than those from Coronach #1. The H/C atomic ratio of the char from Coronach #2 is only slightly higher than that from Coronach #1 (0.43 vs.0.40). Gas analyses will be largely affected by the THF injection for Run P-70. The accuracy of the analyses of the feed and products for Run P-70 is validated by the good elemental balances obtained for the run. The hydrogen balance is slightly high (113.21%); however, this could be due to mistaking water for tar in the cotton wool filter as discussed previously.

4.6 EFFECT OF TEMPERATURE

Five pilot plant runs, P-71, P-72, P-73, P-74, and P-75 were performed using Coronach lignite #2. Run P-75 was done using a newly dried lignite that contained less moisture than the previous lignite (2.77% vs. 9.59%). It was observed that the flow of the low-moisture lignite in the reactor feed line was more fluent than the high moisture one, and that blockages of the pneumatic feeding line hardly occurred. In this pilot plant run P-75, temperatures varied between 550°C and 650°C (normally 615°C), because Run P-73 (at 620°C) was stopped in about one third of normal operation time.

Table 4.9 gives product yields obtained from the pilot plant runs.

Table 4.9. Product yields, pilot plant pyrolysis of Coronach lignite #2, temperature effect.

			maf weight %				
Res.Time (sec)	T (°C)	Run	Gas	Tar	Char	H_2O	Total
0.49	555	P-72 [1]	11.62	6.19	71.99	10.23	100.03
0.43	620	P-73 [1,4]	N.D.	9.28	77.29	6.50	N.D.
0.47	651	P-71 [1]	17.12	15.10	60.93	11.05	104.20
0.50	647	P-65 [2]	16.77	11.37	60.63	10.95	99.72
0.55	646	P-70 [1,3]	23.70	17.31	50.72	10.06	101.78
0.47	712	P-74 [1]	21.29	14.04	56.79	9.29	101.41
0.44	615	P-75 [5]	15.83	12.81	63.99	7.61	100.23

Notes:
1 - Lignite #2 (9.59% moisture, 10.32% ash)

2 - Lignite #1 (12.01% moisture, 15.84% ash)

3 - THF injected in top of reactor

4 - Stopped after 43 minutes (about 1/3 of normal operation time) because of an unsteady gas circulation and a malfunctioning compressor.

5 - Lignite #2 [2.77% moisture, 11.42 (DRY) % ash]

N.D. Not determined

As shown in Table 4.9, Run P-75 gave a much higher tar yield than that of Run P-73 which seems to be reasonable when compared to the results of Runs P-71 (651°C) and P-72 (555°C). The unexpectedly low tar yield in Run P-73 could have been caused by an unsteady gas circulation throughout this run.

The tar yield in Run P-74 (712°C) was lower than that of Run P-71 (651°C). Therefore, in agreement with the previous bench scale unit data, the maximum tar yield was again obtained at approximately 650°C.

The product yields are illustrated in Figure 4.5.

Figure 4.5 indicates that char yields decrease as the temperature rises and that gas yields increase steadily with the temperature. It is also indicated by the data shown in Figure 4.5 that the water produced did not show any trend with temperature, and therefore the increase in gas yield as temperature increased was at the expense of char yield at lower temperature, and both tar and char at high temperatures, in particular over 650°C. The maximum tar yield from this lignite of 15.1% maf at 651°C is one of the highest yields obtained from any low rank Canadian coal.

Table 4.10 shows the composition of gaseous products from Coronach lignite #2.

In the results shown in Table 4.10, it is obvious that considerable amounts of carbon oxides, i.e., CO and CO_2 are

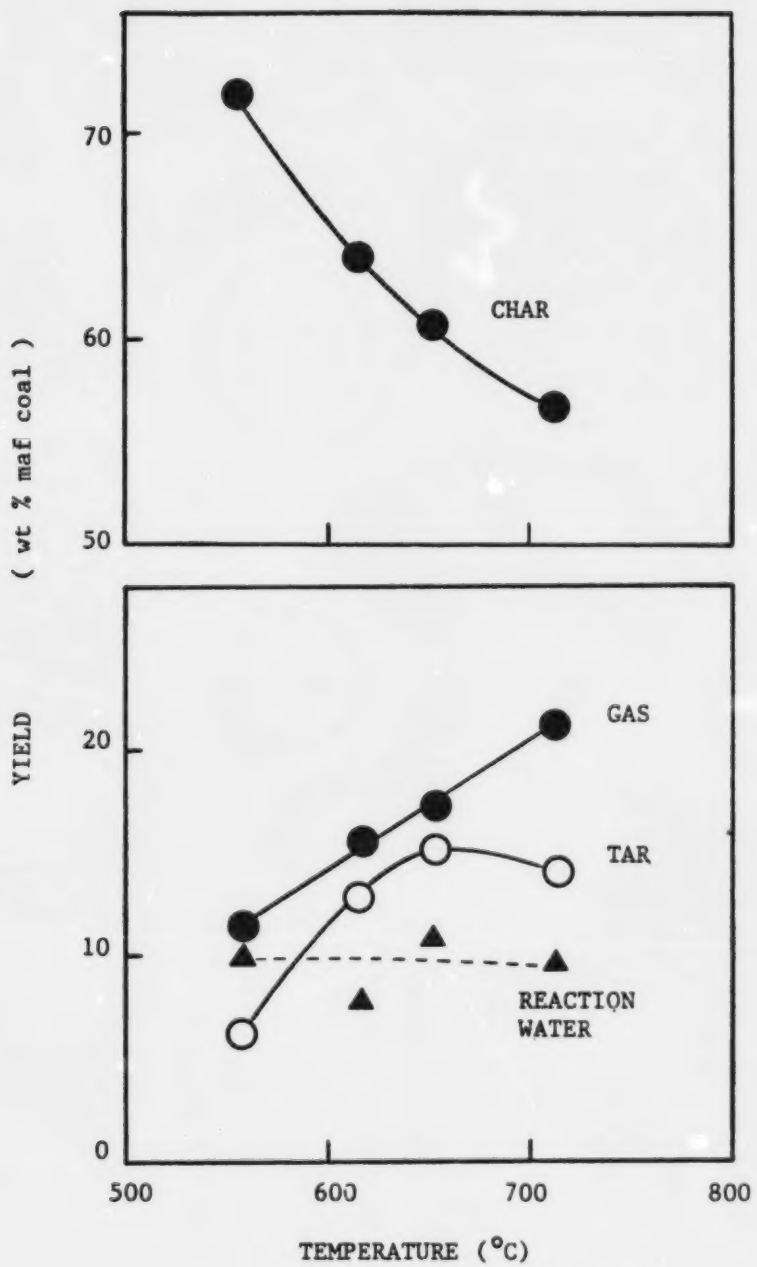


Fig. 4.5 Temperature effect on product yields, pilot plant pyrolysis of Coronach lignite #2, residence time 0.44-0.49s.

Table 4.10. Effect of temperature on composition of gaseous products, pilot plant pyrolysis of Coronach lignite #2.

		P-72	P-75	P-71	P-74
Temperature(°C)		555	615	651	712
Vapour residence time (s)		0.49	0.44	0.47	0.47
Feed rate(kg/h)		1.601	1.633	1.546	1.326
Wt. of coal fed(g)		2935.0	2177.8	2962.9	2939.5
		wt % maf coal			
Gases	H2	0.08	0.06	0.11	0.14
	CO	2.73	5.28	7.86	10.96
	CO2	7.47	8.91	6.91	7.38
	CH4	0.99	1.19	1.76	2.14
	C2H4	0.16	0.29	0.28	0.43
	C2H6	0.08	0.07	0.10	0.12
	C3	0.06	0.02	0.05	0.06
	C4	0.04	0.01	0.05	0.06
	Total	11.62	15.83	17.12	21.29

present in the gaseous products. An estimate at 651°C (P-71) indicates that about 72% of the original oxygen incorporated in the lignite is rejected as CO, CO_2 and water on pyrolysis. At higher temperatures, most of the oxygen in the lignite is removed in this way. It is also observed that at higher temperatures than 650°C, the yield of CO is higher than that of CO_2 possibly due to the equilibrium between the carbon oxides which could be favourable to CO at these high temperatures.

4.7 EFFECT OF FEED RATE

Two pilot plant runs, P-76 and P-77, were performed under different feed rates of 1.124 kg/h and 2.846 kg/h, respectively. A feed rate of approximately 1.5kg/h was used in previous runs and this feed rate was selected empirically to maximize the tar yield in pilot plant pyrolysis.

In Run P-76, a lower feed rate of 1.124 kg/h was used and the reactor temperature was maintained at about 650°C which was determined to give the maximum tar yield in a series of previous runs, P-71 through P-75. The vapour residence time was kept at 0.45 seconds which was approximately the same as that for Run P-71.

In the pilot plant run P-77, a higher feed rate of 2.846 kg/h was used and the reactor temperature was again kept at 650°C. The residence time was also kept at 0.44 seconds. At this higher feed rate, the heater capacity of the reactor reached its limit and the

reactor temperature dropped to 641°C in the first 10 minutes after starting the operation. Thereafter the reactor temperature gradually returned to the control point of 650°C about 25 minutes from starting the feed input.

This temperature change is plotted in Figure 4.6.

As seen in the plot shown in Figure 4.6, the temperature in the fluid bed for the feed rates less than 1.5 kg/h never varies by more than 5°C even at start-up, and after 10 minutes is controlled to 2°C. The temperature in the top of the reactor shows an increase as feed rate increases and it is suspected that this is a thermocouple response effect as gas composition changes. Thus, with the present heater capacity, the feed rate should probably be kept less than 2.846 kg/h to obtain a steady temperature condition, unless a long run is carried out, e.g. 100 minutes or more.

Product yields are given in Table 4.11.

From the results shown in Table 4.11, it is indicated that gas yields increase as the feed rate becomes higher. It is also indicated that the yield is highest in Run P-71, the feed rate of which is 1.546 kg/h. An optimum feed rate to obtain the maximum tar yield again appears to exist just as an optimum reactor temperature exists.

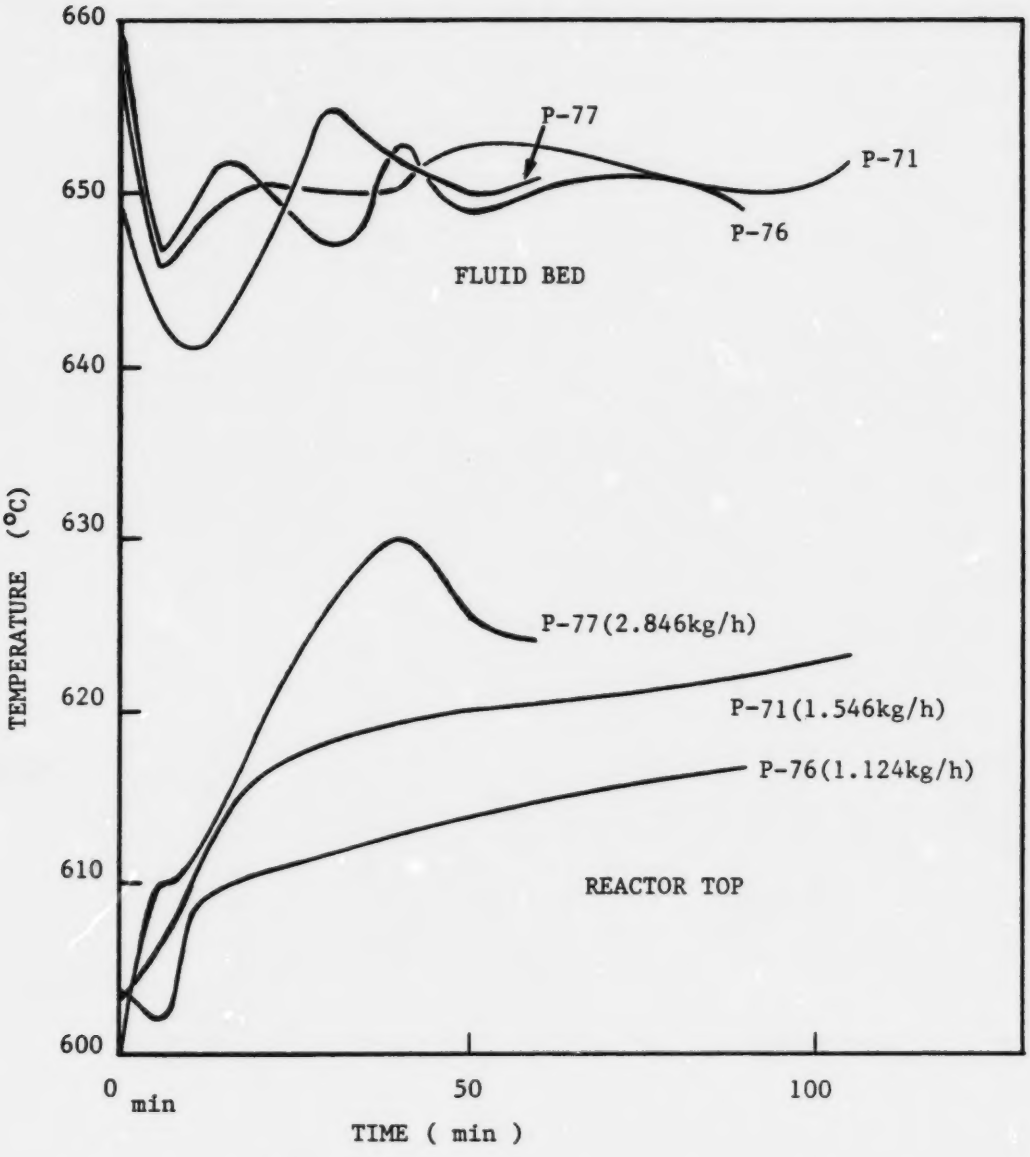


Fig. 4.6 Effect of feed rate on reactor temperatures, pilot plant pyrolysis of Coronach lignite #2, residence time 0.44-0.47 s.

Table 4.11. Effect of feed rate on product yields, pilot plant pyrolysis of Coronach lignite #2.

	P-76	P-71	P-77
Feed rate(kg/h)	1.124	1.546	2.846
Residence time(s)	0.45	0.47	0.44
Temperature(°C)	651	651	648
Wt.of coal fed(g)	1930.0	2962.9	3224.9
Moisture in feed(wt%)	2.77	9.59	2.77
Ash in feed(dry wt%)	11.42	11.42	11.42
	wt % maf coal		
Gas	16.70	17.12	18.82
Tar	13.26	15.10	11.21
Char	64.73	60.93	62.84
Water	8.37	11.05	9.05
Total	103.06	104.20	101.92
Gaseous products			
H2	0.05	0.11	0.13
CO	5.93	7.86	6.72
CO2	7.67	6.91	9.87
CH4	1.64	1.76	1.62
C2H4	0.29	0.28	0.27
C2H6	0.07	0.10	0.09
C3	0.04	0.05	0.06
C4	0.04	0.05	0.05
Total	16.70	17.12	18.82

This fact suggests that the feed rate change may result in a temperature change inside the particle which would consequently affect the tar yield.

Also, the runs at the lowest and highest feed rates had a very low moisture content (2.77%) while the run at 1.5 kg/h which gave the highest tar yield also had a high moisture content in the feed (9.59%). Therefore, Run P-71 was repeated with low moisture content to see if this is indeed a variable which can affect yields. The result of the repeated pyrolysis experiment will be discussed in a later section.

4.8 EFFECT OF RESIDENCE TIME

A pilot plant run P-78 was performed under a short residence time of 0.35 seconds. Short residence time runs are reported to give higher tar yields in pyrolysis of Saskatchewan lignite using bench scale reactors (5). In previous pilot plant runs, a residence time of the range between 0.44 and 0.49 seconds was used normally and this residence time was selected to compare the results with those of bench scale reactors.

In the pilot plant run P-78, gas circulation rate to the reactor was maximized keeping the valves in recycle lines closed throughout the run. A maximum pressure drop of 70 inches H_2O was obtained across the orifice that was placed in a pipe between the compressor and the reactor. The pressure drop across the orifice

was kept at 40 inches H_2O in the previous runs. Thus, the gas circulation rate under this maximum pressure drop is calculated to be 20% to 30% higher than the previous runs.

This pilot plant run was expected to give a higher tar yield, but the result obtained was unsatisfactory because of the difficulty in keeping the higher gas rate throughout the run.

The maximum gas rate was maintained for about 10 minutes after starting the pilot plant operation. The pressure drop across the orifice decreased gradually and reached a lower value of 60 inches H_2O after 20 minutes of operation. This decline in gas circulation rate is attributed to the gas density increase resulting from a production of heavy molecular weight gases, such as CO_2, C_3H_8, C_4H_{10}, etc. Consequently, the gas compressor was unable to maintain the high gas rate, i.e., the short residence time, and this short residence time run was terminated after 24 minutes from the start.

Product yields of Run P-78 are given in Table 4.12, together with those of Run P-79 using the same Coronach lignite #2 sample under the usual residence time of 0.44 seconds.

The tar yield of Run P-78 was almost the same as that of Run P-79 while the gas yield of Run P-78 was lower compared to the usual residence time run P-79.

From the results shown in Table 3.12 , it is observed that the char yield of Run P-78 was unusually high and the total yield was far beyond 100% in the material balance closure of Run P-78. This could be explained by an elutriation of sand particles. This implies that a residence time without any elutriatin of sand particles lies between 0.35 and 0.44 seconds. The nature of the fluid bed reactor generally limits the range of gas residence time which can be varied and still obtain satisfactory fluidizaton in a single reactor.

The "residence time" used here is based on the net empty reactor volume divided by the inlet volumetric gas flow rate at reactor conditions. It is difficult to separate this gas residence time from the effect of char particle residence time. In the fluidized bed for atmospheric flash pyrolysis of various particle sizes of lignite, good mixing should be achieved between the coal particles and the heat carrier sand in order to avoid or reduce secondary reactions leading to the decrease of tar yield. At the same time, the particles formed during the pyrolysis must leave the reactor after a certain residence time. In this binary system, the fluidized bed consists of two species of solids of different density, i.e., coal/char particle and sand particle. When the binary system is fluidized, the segregating tendency of particles of different size or density may lead to a top to bottom variation in concentration.

The data given in Table 4.12 suggest that while the superficial gas velocity of Run P-78 was high enough to blow char particles out of the reactor, this velocity was also high enough to cause the elutriation of some sand.

It is known that, when fine particles are injected into hot gases alone, heating rates of the order of 10^4 °C/s are achieved. In the case of the fluidized bed, collisions between coal and sand particles are likely to increase the rate of heating of the coal particles above that obtained using only a gaseous heat carrier. Hence, although the rate of heating experienced by the coal particles is not known quantitatively, it can reasonably be described as rapid and is likely to be at least 10^4°C/s.

In Run P-78, the residence time of the gas was calculated to be 0.35 seconds, assuming plug flow. However, this residence time would be the minimum residence time of the particles, as they are injected downwards and have to traverse the major part of the bed before elutriation.

MIT workers studied the pyrolysis of Montana lignite by means of a flash heating technique whereby coal particles were held on a heating grid (10). They found the major part of the devolatilization to be complete within 0.1 s at a heating rate of 10^4°C/s. This suggests that, in the fluidized bed, even particles that are directly elutriated after a residence time of about 0.35s would be substantially devolatilized at the reaction temperature.

Table 4.12. Effect of residence time on product yields, pilot plant pyrolysis of Coronach lignite #2.

		P-78	P-79
Vapour residence time(s)		0.35	0.44
Temperature(°C)		656	653
Feed rate(kg/h)		1.840	1.467
Wt. of coal fed(g)		757.5	1893.0
Moisture in feed(wt%)		2.77	2.77
Ash in feed(dry wt%)		11.42	11.42
		wt % maf coal	
Gas		13.72	18.72
Tar		13.36	13.59
Char		77.04*	61.11
Water		10.89	10.11
Total		115.01*	102.93
Note: * Elutriation of sand			
Gaseous products	H2	0.11	0.12
	CO	3.99	6.64
	CO2	6.17	9.05
	CH4	1.85	1.75
	C2H4	0.90	0.34
	C2H6	0.28	0.10
	C3	0.24	0.07
	C4	0.17	0.05
	Total	13.72	18.72

Individual gas yields shown in Table 4.12 indicate that the decrease in the gas yield in the short residence time run P-78 corresponds with the decrease in the yields of carbon oxides. The trend in gas yields is consistent with that reported in the previous experiments using the bench scale reactors (5). It is possible that CO and CO_2 yields are more dependent on the actual char particle residence time than on gas residence time based on superficial velocities.

If the char had a catalytic effect at about 650°C, then the yields of CO and CO_2 could be affected by the catalytic action of char as a gasification promoter. Because the lignite is known to contain alkaline earth cations, the effect of which will be investigated in the following sections, catalytic action associated with these cations is quite likely judging from the trend shown in Table 4.12.

4.9 EFFECT OF MOISTURE CONTENT

A pilot plant run P-80 was performed with Coronach lignite #3 of high moisture content in order to investigate the possibility of the effect of natural moisture content on product yields, particularly on tar yield.

Pilot plant runs P-71 and P-79 were performed, as described in the previous sections of this chapter, with Coronach lignite #2 of high and low moisture content, respectively.

Low-moisture Coronach lignite #2 was dried in an oven with air circulation at 105°C for about 24h, and after drying was kept in a polyethylene bag at room temperature. On the other hand, Coronach lignite #3 was kept open in air at room temperature to bring its moisture content to approximate equilibrium with the laboratory atmosphere. The moisture contents of Coronach lignite #2 and #3 are 27% and 22.77%, respectively. High-moisture Coronach lignite #2 was dried in nitrogen atmosphere at 55°C, as mentioned previously.

Table 4.13 shows the results obtained from three Coronach lignites of different moisture content.

Data obtained from Coronach lignite #2 given in Table 4.13 indicate that the lignite with the high moisture content gave higher tar yield (15.10% vs. 13.59%). Therefore it is likely that low-moisture Coronach lignite #2 was oxidized in the air-circulated oven during drying operation. On the other hand, Coronach lignite #3, the moisture content of which is much higher than Coronach lignite #2, gave a surprisingly high tar yield of 17.32% and this tar yield was one of the highest yields obtained from Coronach lignite.

From these experimental results, it is indicated that water molecules adsorbed on the surface of pores inside the coal particles might prevent oxygen molecules from being adsorbed on the inner surface of coal and hence inhibit the pre-oxidation to some extent.

Table 4.13. Effect of natural moisture in lignite on product yields, pilot plant pyrolysis of Coronach lignites.

		P-79	P-71	P-80
Coal		Coronach #2	Coronach #2	Coronach #3
Moisture in feed(wt%)		2.77	9.59	22.77
Temperature(°C)		653	651	652
Residence time(s)		0.44	0.47	0.45
Feed rate(kg/h)		1.467	1.546	1.590
Wt. of coal fed(g)		1893.0	2962.9	2809.4
		wt % maf coal		
Gas		18.72	17.12	17.06
Tar		13.59	15.10	17.32
Char		61.11	60.93	58.97
Water		10.11	11.05	8.50
Total		102.93	104.20	101.85
Gaseous products	H2	0.12	0.11	0.14
	CO	6.64	7.86	5.81
	CO2	9.05	6.91	8.83
	CH4	1.75	1.76	1.77
	C2H4	0.34	0.28	0.32
	C2H6	0.10	0.10	0.09
	C3	0.07	0.05	0.06
	C4	0.05	0.05	0.04
	Total	18.72	17.12	17.06

Similar results reported in the literature indicate that the principal effect of air oxidation is an increase in micropore surface area arising from reaction with available surface carbon atoms.

Apparently "over-dried" coals appear to be less suitable judging from the viewpoint of attaining high tar yield in "coal pyrolysis".

The pyrolysis behaviour of low rank coals strongly relates to the microstructure of coal, e.g., the porosity, the micropore volume and surface area. Coals can be described as porous heterogeneous, organic rocks containing minor amounts of mineral matter. In addition, coals have interrelated organic, inorganic and physical structures, all of which must be taken into account to explain and predict coal reactivity. Also, as-mined coal contains significant amounts of water, decreasing with increasing rank. It is known that low rank coals contract and crack on drying, and this has been attributed to gel collapse indicating that drying alters the physical structure of low rank coals.

Recently, Suuberg et al. (12) found that the presence of natural moisture in North Dakota lignite appeared to have a significant effect on pyrolysis chemistry, increasing the amount of crosslinking observed at any temperature. They also reported that the undried sample appeared to give slightly higher yields of non-water volatile products. They pointed out that there was a

possibility of moisture being trapped in the pore structure until temperatures as high as 650°C were reached and thus water itself was participating in the pyrolysis process. In their experiment carried out at 650°C, it was estimated that the time between when the experiment was initiated and when the sample reached 650°C was typically only 0.6 s. Therefore they concluded that some water might remain within the pores even at the high temperatures, and thus take part in pyrolysis reactions.

This explanation postulated by Suuberg et al. appears to be affirmed by the present results obtained from Coronach lignite using the Waterloo flash pyrolysis unit.

4.10 PYROLYSIS OF FORESTBURG SUBBITUMINOUS COAL

The pulverized Forestburg subbituminous coal was fed to the pilot plant reactor to investigate the pyrolysis behaviour under rapid heating conditions, which were the same as the previous pilot plant runs carried out with Coronach lignite #3.

Table 4.14 shows the product yields obtained from the pilot plant runs P-86 and P-87, together with the results obtained previously with Coronach lignite #3.

Somewhat higher feed rates of Runs P-86 and P-87 shown in Table 4.14 may be due to the high bulk density of Forestburg subbituminous coal, since coal samples were fed to the reactor by

Table 4.14. Product yields in pilot plant pyrolysis of low rank coals.

	Forestburg subbituminous		Coronach lignite #3	
Run	P-87	P-86	P-85	P-80
Temp.(°C)	582	651	581	652
Res.time(s)	0.47	0.45	0.46	0.45
Feed rate(kg/h)	1.798	1.787	1.635	1.590
Moisture(wt%)	19.05		22.77	
Ash(dry wt%)	8.60		16.21	
Product yields, wt% maf coal				
Gas	11.79	14.89	13.87	17.06
Tar	14.66	17.21	12.47	17.32
Char	72.53*	58.31	67.99	58.97
Water	10.66	12.00	6.37	8.50
Total	109.64*	102.41	100.70	101.85

Note: * Elutriation of sand

Gaseous products, wt% maf coal				
H2	0.13	0.20	0.08	0.14
CO	2.43	5.05	3.26	5.81
CO2	6.98	6.43	8.80	8.83
CH4	1.56	2.32	1.25	1.77
C2H4	0.22	0.37	0.23	0.32
C2H6	0.23	0.27	0.12	0.09
C3	0.14	0.14	0.08	0.06
C4	0.10	0.11	0.06	0.04
Total	11.79	14.89	13.87	17.06

a volumetric feeder. In the previous study with Coronach lignite #2, however, the effect of feed rate on tar yield was found to be less significant compared with the other operating conditions. Hence it could be that the slight difference in feed rate with Forestburg subbituminous coal is not seriously detrimental to the tar yield in the pilot plant pyrolysis.

From the results shown in Table 4.14, it is indicated that Forestburg subbituminous coal gives a tar yield similar to Coronach lignite #3 at about 650°C. This result is quite surprising because these two coals have a considerably different analytical composition, particularly in the proximate analysis shown in Table 4.2.

At about 580°C, however, Forestburg subbituminous coal gave a slightly higher tar yield than Coronach lignite #3.

In contrast to the proximate analysis, the results of ultimate analyses of these two coals show that they have quite similar elemental composition except for nitrogen content and that they have the same H/C atomic ratio. It is interesting to note that the ash content of Coronach lignite #3 is much higher than that of Forestburg subbituminous coal (16.21 dry% vs. 8.60 dry%), because, as discussed later, metal cations contained in low rank coal play an important role in pyrolysis reaction occurring in the coal. As regards the tar yield of Forestburg subbituminous coal, it is noteworthy that the tar yield maximum occurred at about 650°C,

which is close to the temperatures of the pore volume maxima reported by Singla et al. (13) in the study on changes in the pore properties during carbonization of this coal.

Product gas compositions from both coals shown in Table 4.14 indicate that Forestburg subbituminous coal gives a slightly lower gas yield at each temperature and that the decrease in gas yields is largely caused by lower CO and CO_2 yields.

Although how CO and CO_2 are released from the precursors still remains uncertain, it has been shown by other workers that carboxyl and carbonyl groups are major potential precursors of carbon oxides and that these oxygen-containing functional groups are eliminated above 550°C.

The results in Table 4.14 also indicate that the lower yields of gas from Forestburg subbituminous coal are partly offset by higher yield of H_2O. This fact suggests that the thermal decompositions of Forestburg subbituminous coal and Coronach lignite #3 might have different reaction paths, particularly causing different partitioning of oxygen between the pyrolysis products.

5. ROLE OF EXCHANGEABLE CATIONS IN PYROLYSIS OF LIGNITE

5.1 INTRODUCTION

The role of exchangeable cations on pyrolysis of low rank coals has been extensively investigated in the experimental study reported in our previous contract using the bench scale fluidized bed reactors [Scott (9)]. Many studies have shown that lignites react quite differently than coals of higher rank when subjected to pyrolysis processes. The behaviour of lignites is believed to be greatly influenced by the inorganic constituents present. The most distinctive feature of the inorganic constituents of lignites is the large concentration of exchangeable metal cations. These cations are mainly alkali and alkaline-earth metals associated with the carboxyl groups present in lignites. Experimental work on the acid washing of lignites has been reported in several studies (14)(15)(9). In brief, lignites contain high levels of oxygen, of which about one-third is present as carboxylic acid groups. Many lignites contain cations, e.g., sodium, potassium, magnesium, calcium that have been exchanged with carboxylic protons. It has been found that, all else being equal, the tar yield of pyrolysis increases as the cation content decreases. Acid washing replaces the cation with a proton, and coals so treated give the higher tar yields as already noted. Also, it has been shown previously (9), that the maximum tar yield increased as the atomic H/C ratios of the coals increased.

5.2 EXPERIMENTAL

5.2.1 Exchangeable Cation Determination

The procedure for the determination of exchangeable cations was adapted from the study of Morgan, Jenkins, and Walker (15). Coronach lignite #3 was subjected to ion exchange with ammonium acetate (NH_4Ac) in order to selectively remove only the exchangeable cations and leave essentially intact the discrete mineral matter.

A 1.2N NH_4Ac solution was prepared and adjusted for a pH of 7.1. 1.07 g of Coronach lignite #3 was mixed with 50 ml of 1.2 N NH_4Ac and stirred at room temperature for 19 hours.

The coal was then filtered, rinsed with fresh 1.2N NH_4Ac solution and subjected again to a 2.5 hour exchange with another 50 ml of fresh solution, followed by the same washing procedure. Three more exchange cycles were carried out with successive exchange times of 2.25, 17.75 and 4.25 hours. The filtrates were collected after each cycle and analyzed for the exchanged Ca, Mg, Na and K by atomic absorption spectroscopy. The instrument used was a Perkin-Elmer atomic absorption spectrometer model 303. The samples were diluted so that the concentration of the specific cation being analyzed was within the sensitivity range of the instrument. This meant that sample concentrations had to be 1-10 ppm Ca for Ca analysis, 1-10 ppm K for K analysis, 0.1-2.0 ppm Mg

for Mg analysis, and 0.3-3.0 ppm Na for Na analysis. To overcome vapourization and ionization interferences a 5 percent La solution in 25 percent (V/V) HCl was prepared and added to the diluted samples. This resulted in all samples containing one percent La. Corrections were made for cations present in the distilled water and in the La solution.

5.2.2 Acid Washing

A sample of 12,128 grams of Coronach lignite #3 was acid washed in 60 L of HCl solution, the pH of which was kept at approximately 2.5. The coal and acid solution was stirred continuously for 6 hours. After that time, the slurry solution was allowed to settle down for 65 hours in an attempt to completely precipitate small coal particles.

After decanting the acid solution, the coal was washed with about 40 L of distilled water. Each solution was filtered and checked for chloride ions by the addition of a drop of silver nitrate to the filtrate. If a cloudy white precipitation was formed, the coal was washed again. Eventually, the coal was washed eight times; six times with distilled water and twice with deionized water. Each washing solution was collected and analyzed for cation contents.

When washing with deionized water, it was observed that the slurry solution turned brown. This brownish colour of the solution was due to a number of small particles. These small

particles passed through an 8 μm filter paper, but they were filtered off by a 2.5 μm filter paper. Thus, the size of these particles is estimated to be between 2.5 μm and 8 μm. Although this brownish suspension (humic acid?) has not been elucidated precisely, it should be noted that the small particles held in suspension have a very slow settling rate which causes a difficulty in the separation of coal and deionized water on the basis of density.

The acid washed coal was dried under an air stream at room temperature in an attempt to bring the moisture content to approximate equilibrium with the laboratory atmosphere in order to minimize the gain or loss of the moisture content during sampling operations.

5.3 RESULTS AND DISCUSSION

5.3.1 Exchangeable Cation Content of Parent Coal

In the present experiment, the ion exchange reaction by ammonium acetate (NH_4Ac) was used for the determination of each cation content of Coronach lignite #3.

The progress of the exchange reaction for each cation is illustrated in Figure 5.1. The results given in Figure 5.1 indicate that Ca and Mg are the predominant cations in this lignite. It is also indicated that the removal of these cations are almost completed within the first three cycles.

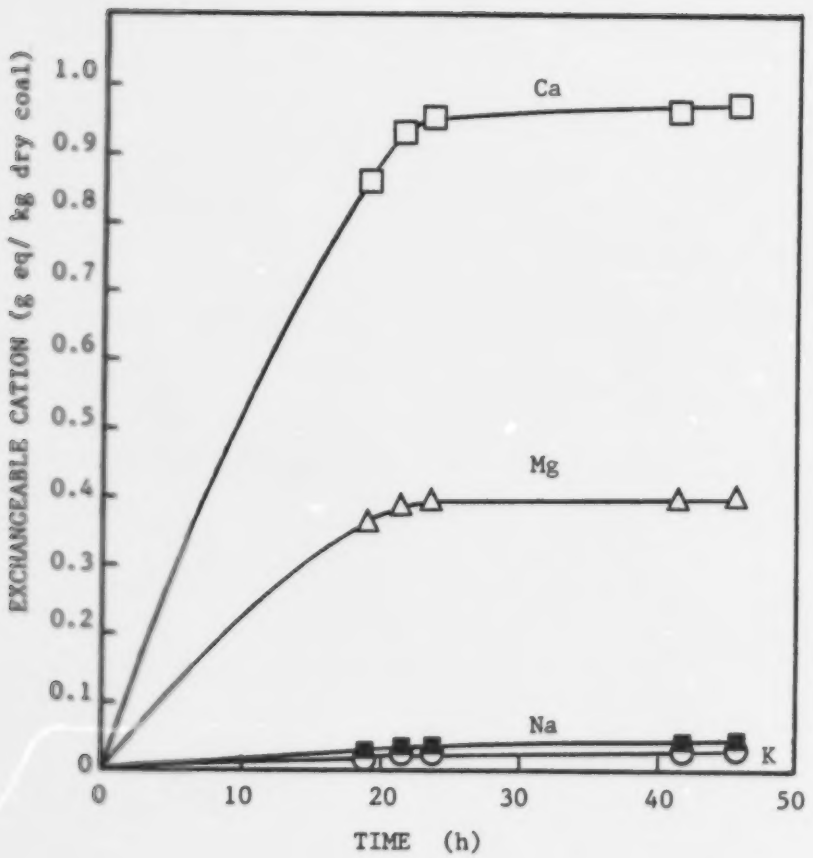


Fig.5.1 Release of exchangeable cations from Coronach lignite #3 during NH4Ac treatment.

Table 5.1 gives the exchangeable cation determination results obtained from Coronach lignite #3. For comparison, results of cation analysis of Estevan lignite #4 are also shown. Properties of these lignites were previously given in Tables 4.2 and 4.3.

The ash content of Coronach lignite #3 is more than twice as high as that of Estevan lignite #4 (16.21 dry% vs. 6.70 dry%) and coincidently the exchange cation contents of Coronach lignite #3 is approximately two times higher than those of Estevan lignite #4 except for Na. On the other hand, as previously shown in Table 4.1, the ultimate analyses of these lignites indicate that they have quite a similar elemental composition.

The concentrations of exchangeable cations determined for these lignites are very similar to the results for American lignites reported by Morgan et al. (15).

5.3.2 Acid Washing Test

For acid washing treatment, Coronach lignite #3 was chosen, because it was previously well characterized by pilot plant pyrolysis and because it contains a large quantity of ion-exchangeable cations.

Acid washing of Coronach lignite #3 was carried out to obtain a sufficient amount of acid washed coal as a feedstock to the pilot plant reactor.

Table 5.1. Exchangeable cations extracted by ammonium acetate.

(1) wt % dry coal
(2) g eq / kg dry coal

	Coronach lignite #3		Estevan lignite #4 *	
	(1)	(2)	(1)	(2)
Ca	2.03	1.01	1.07	0.53
Mg	0.49	0.40	0.25	0.21
Na	0.09	0.04	1.21	0.53
K	0.12	0.03	0.06	0.02
Total	2.73	1.48	2.59	1.29

Note: * Data from Scott(1986),Contract OST 84-00007.

The extracts for each acid treatment were saved for cation analysis. The metal contents in the acid washed extracts were determined and these quantities were subtracted from the metal contents of the raw coal to obtain the values for the acid washed coal sample.

The results are given in Table 5.2.

Table 5.2 shows metal cation contents of acid washed Coronach lignite #3, together with the previous results from Estevan lignite #4 by Scott (9). From Table 5.2, it is observed that the metal contents of acid washed coals prepared under the same acid washing condition, i.e. pH = 2.5 HCl, are almost the same values except for the Na contents. In the acid washing of Coronach lignite #3, the removal rates of Ca, Mg, Na and K were 84, 97, 78 and 19%, respectively on the basis of exchangeable cation contents of the original coal extracted by NH_4Ac. These values are in good agreement with those of Estevan lignite #4.

The removal of ash was almost exactly 50 % of that in the original Coronach lignite #3, as shown in Table 4.2.

In the previous experiments reported by Scott (9), it was suggested that the degree of cation removal might be affected both by solution equilibrium and to a lesser degree by the particle size distribution. Almost the same metal cation contents of these lignites when treated under similar conditions might confirm the possible effect of solution equilibrium on the degree of cation

Table 5.2. Metal cation contents of acid washed lignites, pH=2.5, HCl.

(1) weight % dry coal
(2) gram equivalents per kg dry coal

	Coronach #3		Estevan #4 *	
	(1)	(2)	(1)	(2)
Ca	0.32	0.16	0.33	0.16
Mg	0.01	0.01	0.04	0.03
Na	0.02	0.01	0.47	0.20
K	0.10	0.02	0.05	0.01
Total	0.45	0.20	0.89	0.40

Note: * Data from Scott(1986),Contract OST84-00007.

removal. The lower sodium content of Coronach lignite #3 compared to Estevan lignite #4 could be attributed to a different depositional history. Therefore, a knowledge of depositional environments of lignite would be helpful for studies on the role of inorganic constituents in the lignite and eventually for the development and utilization of the coal deposit.

5.3.3 Pyrolysis of Acid Washed Lignite

Raw and acid washed lignites were subjected to pilot plant pyrolysis in order to investigate the effect of acid washing on product yields.

The experimental procedure consisted of pyrolysis using the pilot plant reactor equipped with insulated cyclone and cold char pot. Vapour product collection consisted of a system of two condensers and a cotton wool filter connected in series.

Gaseous products were analyzed by gas chromatography. Liquids were washed out of the system of two condensers using tetrahydrofuran (THF). The solvent was evaporated at about 65°C and 20 inches Hg vacuum, and the liquid product was then weighed and stored in a refrigerator prior to further analyses.

Table 5.3 gives results of pyrolysis runs with the acid washed lignite (Runs P-82, P-83 and P-84) as well as Runs P-80 and P-85 with untreated lignite. The major effect of the acid washing is the increase in tar yield with a parallel reduction of gas and

Table 5.3. Effect of acid washing on product yields, pilot plant pyrolysis, Coronach lignite #3, pH=2.5, HCl.

	Acid washed			Original	
	P-84	P-82	P-83	P-85	P-80
Temperature(°C)	553	652	732	581	652
Residence time(s)	0.50	0.46	0.41	0.46	0.45
Feed rate(kg/h)	1.657	1.535	1.577	1.635	1.590
Moisture(wt %)	20.91	20.91	20.91	22.77	22.77
Ash(dry wt %)	8.83	8.83	8.83	16.21	16.21
Product yields, wt % maf coal					
Gas	13.85	16.55	21.07	13.87	17.06
Tar	15.20	19.95	17.53	12.47	17.32
Char	63.18	57.31	55.69	67.99	58.97
Water	9.25	7.41	12.22	6.37	8.50
Total	101.48	101.22	106.51	100.70	101.85
Gaseous products, wt % maf coal					
H2	0.07	0.11	0.17	0.08	0.14
CO	4.14	5.93	9.69	3.26	5.81
CO2	7.39	8.38	8.29	8.80	8.83
CH4	1.31	1.59	2.05	1.25	1.77
C2H4	0.54	0.33	0.57	0.23	0.32
C2H6	0.17	0.08	0.12	0.12	0.09
C3	0.14	0.07	0.09	0.08	0.06
C4	0.09	0.06	0.09	0.06	0.04
Total	13.85	16.55	21.07	13.87	17.06

char yields. A lower CO_2 yield accounts for part of this decrease in gas yield. These trends are in good agreement with results obtained from Estevan lignite #4 using the bench scale reactor [Scott (9)].

5.3.4 Tar Yields

Figure 5.2 illustrates the results of tar yields from Coronach lignite #3, together with those from the previous pilot plant runs with Coronach lignite #2 which would be helpful in interpreting the data from Coronach lignite #3.

In the previous results from Coronach lignite #2, it was suggested that tar yields were strongly temperature dependent. Figure 5.2 confirms the dependence of tar yields upon temperature with respect to the acid washed Coronach lignite #3. Figure 5.2 also indicates that maximum tar yields are obtained at about 650°C in all cases. The maximum tar yield of 19.95 % in Run P-82 was one of the highest yields obtained from this lignite and this yield is comparable to the high tar yields reported by other researchers with Australian brown coal using a small-scale fluidized bed reactor or with Wyoming subbituminous coal using a process development unit.

The tar yields from acid washed Coronach lignite #3 were higher than those of raw Coronach lignite #3 at the temperatures tested. The gain in tar yield at 652°C was 2.63 wt% maf coal and

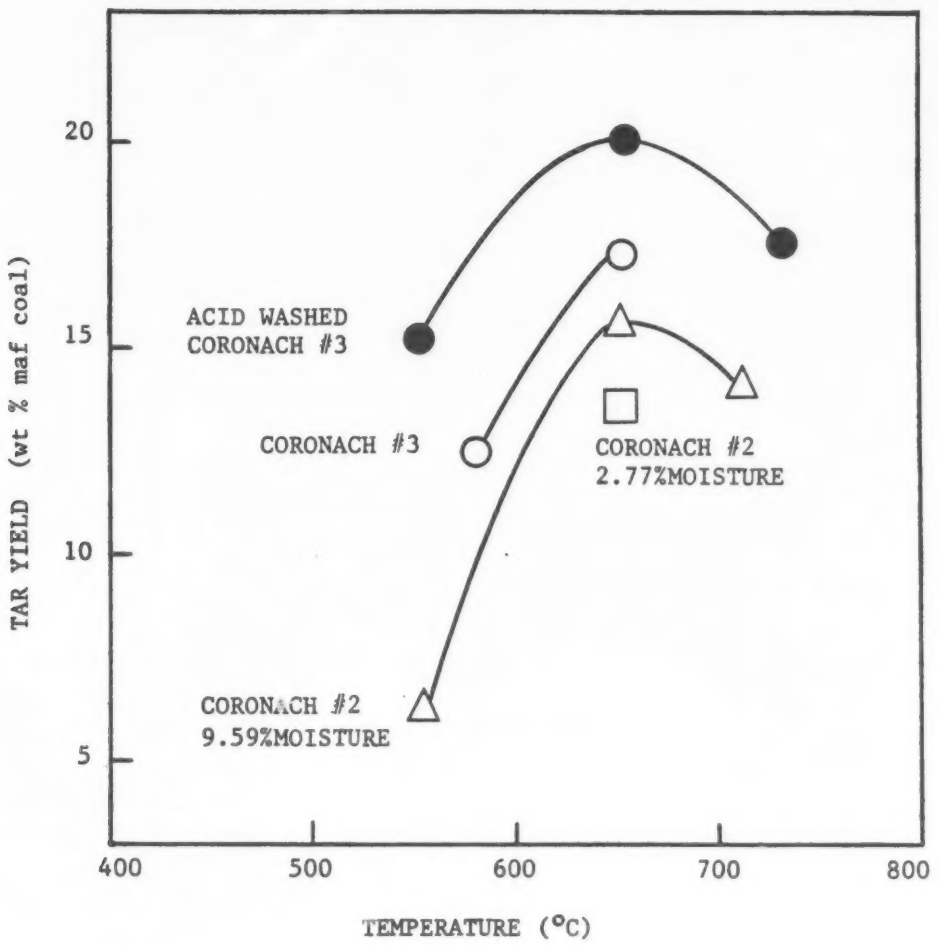


Fig.5.2. Tar yields from Coronach lignites, pilot plant pyrolysis.

this gain was observed to increase with decreasing temperature from 650°C to 550°C.

5.3.5 Char and Gas Yields

Figure 5.3 illustrates the char yields from Coronach lignite #3, together with those from Coronach lignite #2. In Figure 5.3, apparent char yields were corrected assuming the difference of total yields from 100% to be the elutriation of sand particles from the fluidized sand bed. According to the corrected char yields, it is obvious that char yields are decreased by acid washing. The degree of the decrease in char yields appears to become more significant at lower temperatures.

Total gas yields are illustrated in Figure 5.4, together with the yields of CO and CO_2. From the results shown in Figure 5.4, it is indicated that total gas yields increase rectilinearly with temperature. However, the influence of acid washing on the total gas yields appears to be less significant especially at temperature zone over 650°C. While carbon monoxide yields increase rectilinearly with temperature, carbon dioxide yields appear to remain comparatively unchanged at temperatures tested. This somewhat peculiar behaviour of carbon dioxide might be ascribed to the equilibrium between carbon monoxide and carbon dioxide, which could be favourable to carbon monoxide at these high temperatures. It is interesting to note that the carbon dioxide yields were decreased by acid washing while the carbon monoxide yieldsincreased.

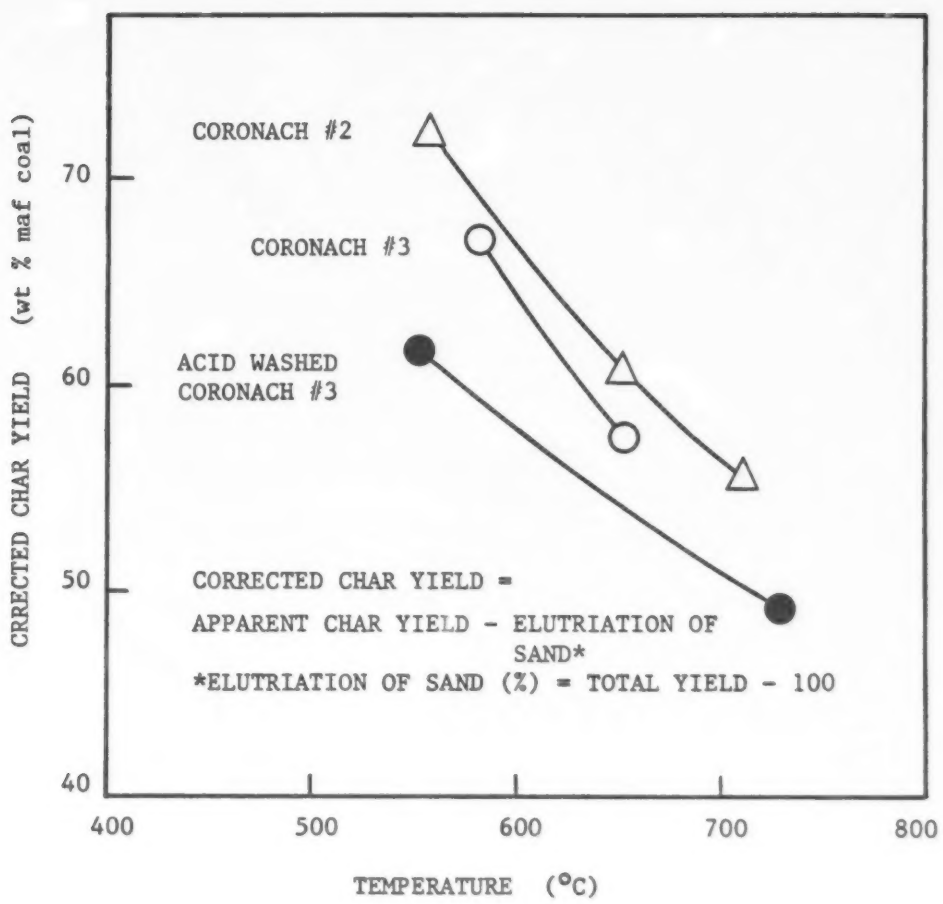


Fig.5.3. Char yields from Coronach lignites, pilot plant pyrolysis.

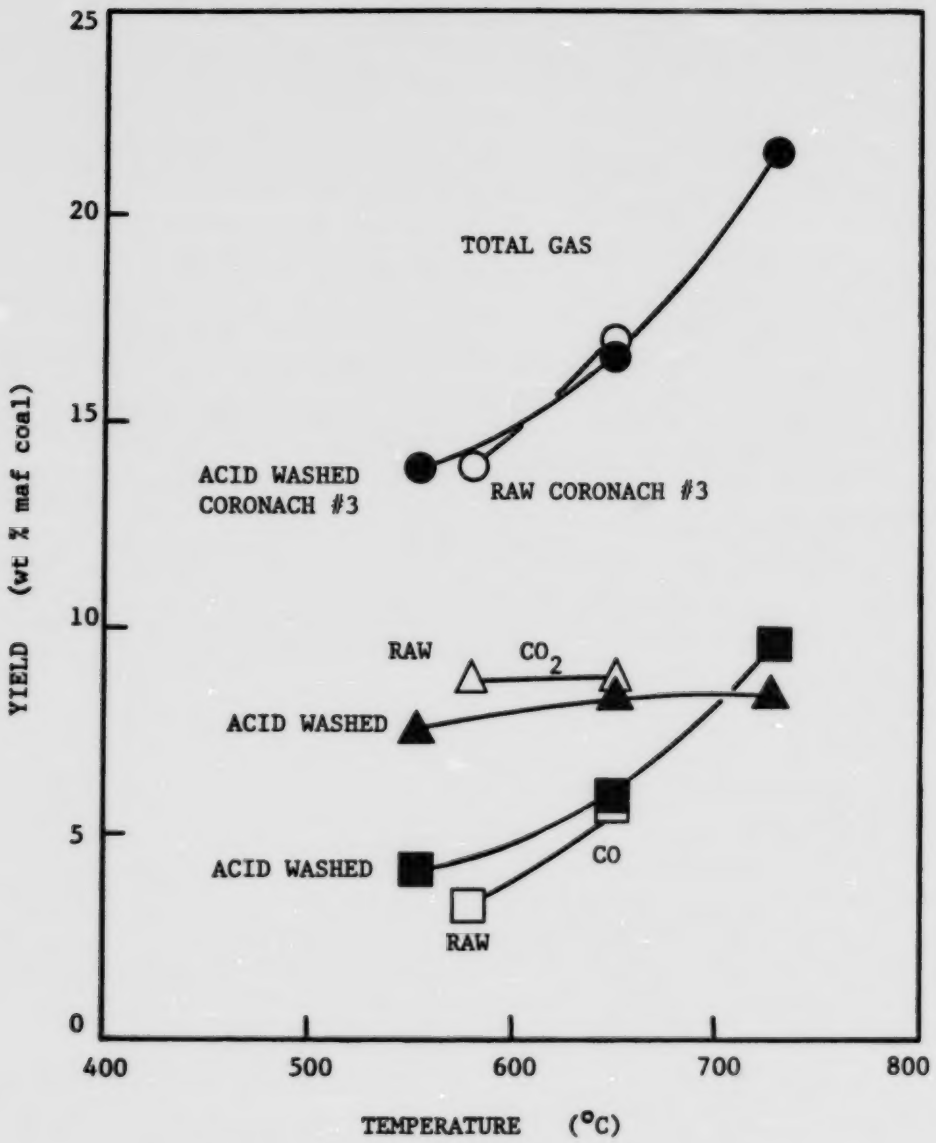


Fig. 5.4. Gas yields from Coronach lignites, pilot plant pyrolysis.

In the previous experiments performed using the bench scale reactor, it was suggested that inhibition of the water gas shift reaction could be responsible for the higher CO/CO_2 ratio and lower H_2 yield in the acid washed lignite compared to the original lignite. This postulation can be supported by the results in Table 5.3 indicating higher CO/CO_2 ratios and lower H_2 yields in the case of pyrolysis of acid washed lignite.

The acid washed lignite was also pyrolyzed at about 550°C in Run P-84. The lower temperature resulted in lower gas and tar yields and higher char yield.

5.3.6 Improvement in Tar Yield

The effect of acid washing on a Saskatchewan lignite was previously investigated by Scott et al. (5). The results showed that the improvement in tar yield obtained with Estevan lignite #3 agreed well with a correlation derived from the results obtained with other acid washed lignites or brown coals.

Figure 5.5 illustrates the correlation for acid washed lignites, together with the results obtained with Coronach lignite #3.

The results shown in Figure 5.5 appear to suggest that the maximum tar yield from acid washed Coronach lignite #3 is in good agreement with what would be estimated from results obtained with other lignites or brown coals. Figure 5.5 also indicates that the

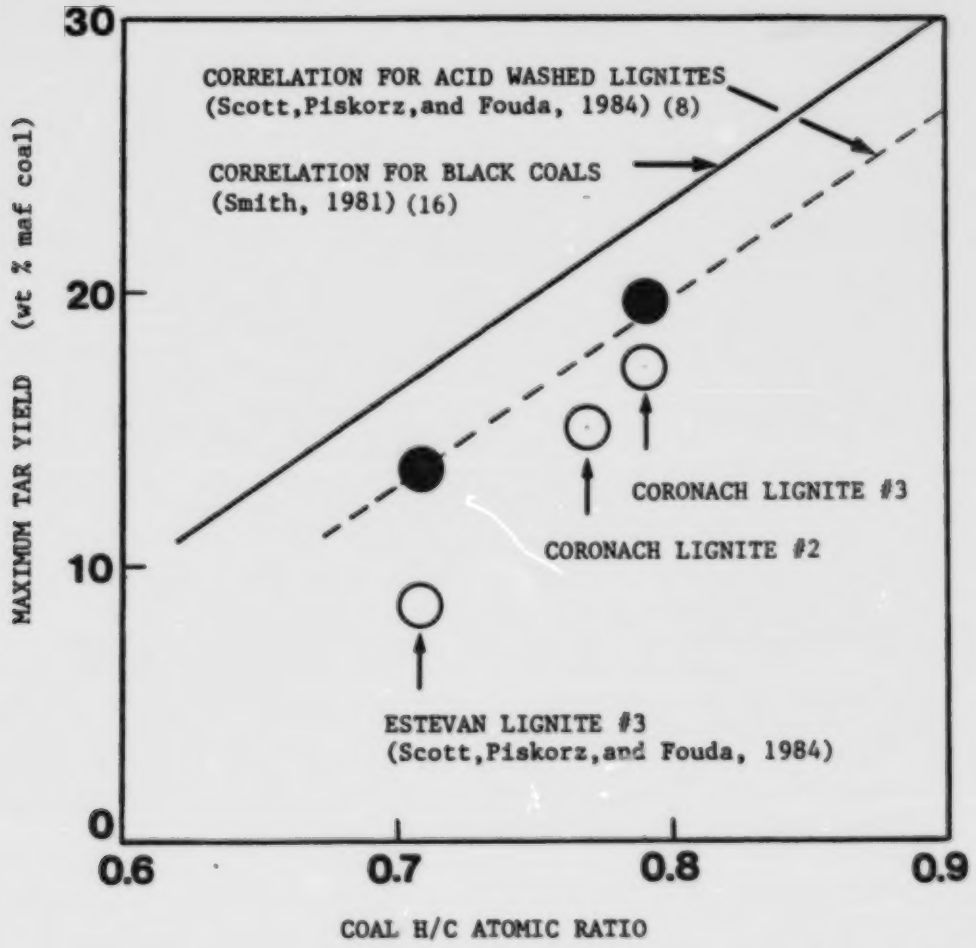


Fig.5.5. Correlation for acid washed lignites

● acid washed lignites

○ original lignites

maximum tar yields from raw Coronach lignites are comparatively higher than that of Estevan lignite. The effect of natural moisture associated with original lignites upon tar yields might be one of many possibilities which explain the deviation in the maximum tar yields obtained with the raw lignites. As suggested previously drying of coal may result in a reduction in reactivity of the coal. The difference in reactivity of both dried and undried coals might be caused by some reactions taking place during the coal drying process.

It is hoped that further work would be carried out to elucidate the effect of moisture on tar yields for the purpose of improving the conversion of low rank coals to liquid products.

5.3.7 Composition of Gaseous Products

Typical reactions between gaseous products taking place in a series of interesting processes are formally represented by:

1. Boudouard reaction

$$C + CO_2 \longrightarrow 2CO \qquad [+167.9\ kJ/mol] \qquad (5.1)$$

2. Carbon-steam reaction

$$C + H_2O \longrightarrow CO + H_2 \qquad [+135.7\ kJ/mol] \qquad (5.2)$$

3. Shift reaction

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad [-32.2\ kJ/mol] \qquad (5.3)$$

The bracketed terms designate the accompanying heat release (-) or heat absorption (+) per mole.

Generally, water can participate in the carbon-steam reaction and/or the shift reaction, as shown above. Although the yields of pyrolytic water shown in Table 5.3 appear to present no significant tendencies in relation to the hydrogen and carbon oxides yields, the low water yield observed in Run P-82 with the acid washed lignite may suggest that reactions of water play some part in the experimental results obtained from flash pyrolysis. It is also noteworthy that Ca and Mg in the original lignite do not seem to be acting as gasification catalysts, as seen in Table 5.3.

Table 5.4 shows the gas compositions on a basis of volumetric percentage.

It is interesting to mention particularly the difference between the gas compositions of the two runs P-84 at 553°C and P-82 at 652°C. The results in Table 5.4 indicate that Run P-84 yielded a higher percentage of CO_2 (36.1 vol % vs. 31.6 vol %), a lower percentage of CO (32.1 vol % vs. 38.5 vol %) and a slightly lower percentage of hydrogen (7.7 vol % vs. 10.0 vol %). The same trend is observed when comparing the gas compositions of the runs with the original lignite, P-85 at 581°C vs. P-80 at 652°C. These results again confirm the fact that the Boudouard reaction and the carbon-steam reaction could be dominant at higher temperatures while the shift reaction would become less significant at these high temperatures.

Table 5.4. Composition of gaseous products

	Acid washed			Original	
	P-84	P-82	P-83	P-85	P-80
Temperature(°C)	553	652	732	581	652
Residence time(s)	0.50	0.46	0.41	0.46	0.45
Feed rate(kg/h)	1.657	1.535	1.577	1.635	1.590
Gaseous products, vol %					
H2	7.7	10.0	11.1	8.4	11.42
CO	32.1	38.5	44.8	26.2	34.6
CO2	36.1	31.6	24.1	44.6	33.1
CH4	17.7	17.0	16.4	17.4	18.2
C2H4	4.1	2.0	2.6	1.8	1.9
C2H6	1.2	0.5	0.3	0.9	0.5
C3	0.8	0.3	0.3	0.4	0.2
C4	0.3	0.1	0.2	0.2	0.1
Total	100.0	100.0	100.0	100.0	100.0

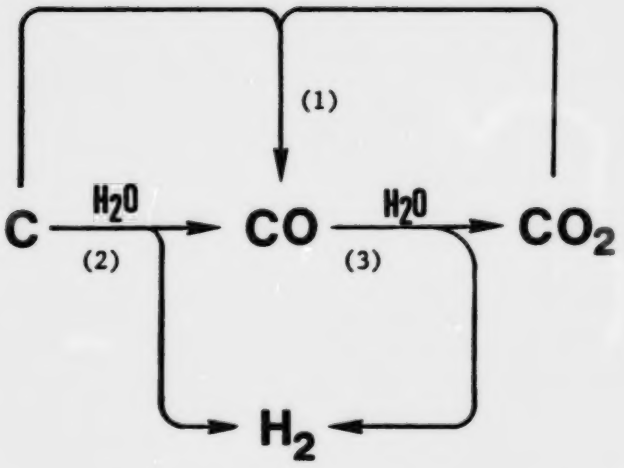
As mentioned above, the higher CO/CO_2 ratio of acid washed lignite gases can be explained by the promotion of the Boudouard reaction and the carbon-steam reaction as well as by the inhibition of the water gas shift reaction.

Figure 5.6 shows interacting gas reaction processes which generally occur in pyrolysis of coal.

In Figure 5.6, it can be interpreted that at higher temperatures the Boudouard reaction (1) and the carbon-steam reaction (2) are more dominant compared to the shift reaction (3). Consequently, CO production is promoted.

It is also obvious that natural water present in original coal and/or reaction water produced during pyrolysis of coal can participate in the carbon-steam reaction and also in the shift reaction.

Suuberg et al. (12) reported the possibility of some water remaining within the pores at the higher temperatures and thus taking part in pyrolysis chemistry. Scott (9) reported increasing CO with decreasing CO_2 and H_2 yields as cations are removed by acid washing. Coupling the possibility postulated by Suuberg et al. with the experimental evidence reported by Scott suggests that cations can participate in pyrolysis reactions and in particular catalyze the shift reaction.



(1) BOUDOUARD REACTION (+167.9 kJ/mol)

(2) CARBON-STEAM REACTION (+135.7 kJ/mol)

(3) SHIFT REACTION (-32.2 kJ/mol)

Fig.5.6. Typical gas reactions taking place during pyrolysis of coal.

6. CHARACTERIZATION OF LIQUEFACTION PRODUCTS

6.1 INTRODUCTION

Liquids obtained from coal by pyrolysis are known to be extremely complex mixtures. Many techniques and methods have been applied to the characterization of the pyrolysis liquids. Depending on the end use of the analytical results, a choice between miscellaneous analytical techniques must be made by comparing the advantages and drawbacks. In the case considered here, the objective is to determine analytical procedures that would permit a significant comparison between coal derived liquids obtained under different operating conditions with several kinds of feedstocks.

Because this was a preliminary investigation, much of the experimental work was sequential as the understanding of the analytical results evolved. Therefore it seems to be more appropriate to discuss each set of results in turn, as they are presented.

In the present work, two types of methods have been used:

1. Separation methods
2. Identification methods.

The separation methods include extraction methods using selective solvents, i.e., pentane, toluene and methanol.

The identification methods include mass spectrometry (MS) as well as high resolution gas chromatography. These can be applied after a more or less elaborate fractionation process.

6.2 SOLVENT FRACTIONATION

6.2.1 Preliminary Experiments

Several samples of the coal pyrolysis tars obtained from the pilot plant tests were analyzed by solvent fractionation using the scheme shown in Figure 6.1.

The results of the solvent fractionation are given in Tables 6.1 and 6.2.

The results shown in Table 6.1 indicate that total recovery percentages in the solvent fractionation ranged between 81% and 85%. This result suggests that some sort of light hydrocarbons, the boiling points of which are similar to that of toluene, exist in tars. Thus the lost portions are assumed to be some light hydrocarbons in the toluene-soluble pentane-soluble fractions (oils).

Therefore, it is recommended that, when identifying the ingredients in the lost portion, a whole tar should be used. The ingredients in the lost portion could be determined from analyses of both tars and the oil fractions by GC/MS.

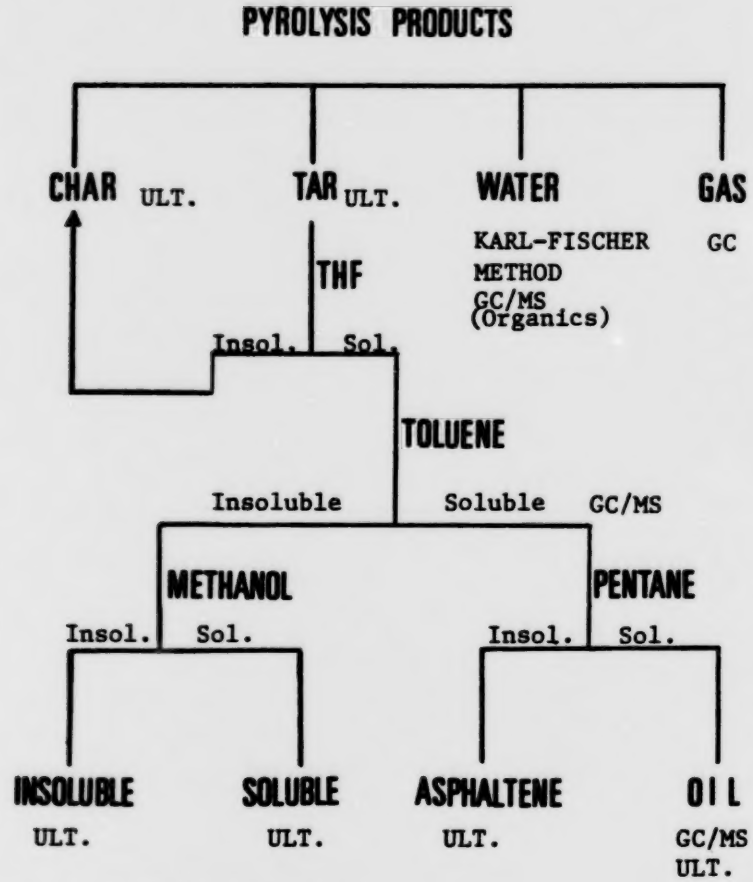


Fig.6.1. Solvent fractionation and identification schematic.

Table 6.1. Solvent fractionation of tars from Coronach lignite #2, preliminary test, method by Mima et al.(1978).

T (°C)	Run	Toluene Soluble		Toluene Insoluble (Preasphaltene)	Recovery[1]
		Pentane Soluble (Oil) %	Pentane Insoluble (Asphaltene) %	%	%
555	P-72	7.1	48.9	28.4	85.2
651	P-71	17.0	48.0	18.8	83.8
712	P-74	5.6	55.2	20.9	81.7
615	P-75	13.6	47.8	23.1	84.5
649	P-70	11.3	40.7	30.7	82.7

Note: 1 - The lost portion is assumed to be some light hydrocarbons in the pentane soluble fraction.

Table 6.2. Methanol extraction of preasphaltene, preliminary test, pilot plant pyrolysis, Coronach lignite #2.

T °C	Run	Methanol Soluble	Methanol Insoluble	Recovery[1]
		%	%	%
555	P-72	47.4	37.6	85.0
651	P-71	30.5	51.8	82.3
712	P-74	48.1	44.6	92.7
615	P-75	44.4	50.7	95.1

Note: 1 - The lost portion is assumed to be some low-boiling-point compounds in the methanol soluble fraction.

The toluene insoluble fractions (preasphaltenes) were fractionated further using methanol, because this fraction could contain lower molecular weight polar oxygenated compounds formed from the humic acid portions of the lignite. As the results in Table 6.2 show, 45% to 50% of the preasphaltene is indeed methanol soluble, that is, about 10% of the tar product.

6.2.2 Modification of Solvent Fractionation

The procedure of solvent fractionation was changed to avoid polymerization and condensation reactions between reactive components in tar products.

The original method of solvent fractionation proposed by Mima et al. (17) is briefly given in an itemized form on the following page. In this method, some insoluble matter was formed in the toluene soluble fraction when evaporating toluene under heating conditions. This insoluble matter was highly viscous and was obviously formed by polymerization or condensation between toluene soluble materials. Since heating conditions are likely to accelerate these reactions, every heating step was eliminated from the procedure of solvent removal. Thereafter the solvent removal was performed at room temperature in a draught chamber under an air stream.

It should be noted that the method of solvent fractionation described by Mima et al. aimed at the determination of weight

Solvent Fractionation Method (Mima et al.)

Determination of Insolubles, Asphaltenes and Oils in Coal-Derived Liquids*

Toluene Insoluble (Preasphaltene)

1. Weigh to the nearest 0.1 mg a 250 ml beaker containing a glass stirring rod.
2. Add about 20 g of tar and weigh to the nearest milligram.
3. Add 150 ml of toluene and mix thoroughly.
4. Filter through a tared Soxhlet thimble into a tared 400 ml beaker.
5. Place the thimble in the Soxhlet apparatus and extract with 300 ml of fresh toluene over night.
6. Dry toluene insolubles in the oven at 105°C for two hours.
7. Calculate the percentage of toluene insolubles (A%).
8. Calculate the toluene solubles by subtracting A from 100% (B% = 100% - A%).

Asphaltene

1. Quantitatively transfer the extract from the Soxlet extraction apparatus to the 400 ml beaker containing the first portion of toluene soluble material.
2. Evaporate toluene until the weight of tolyene solubles is within 10 mg of the weight calculated by subtracting the weight of the toluene insolubles from the sample weight, using a rotary evaporator (65°C, 25 in. Hg) and a hot plate.
3. Add 250 ml of n-pentane while stirring vigorously.
4. Filter the suspension of asphaltenes through a tared fluted filter paper.
5. Wash the gummy asphaltic material until becoming brittle.
6. Dry the paper and asphaltenes in a vacuum oven at 60°C for one hour.
7. Calculate the percentage of asphaltenes (C%).

Oil

Subtract C% from B% to obtain percentage of oil.

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* Mima, M.J., Schultz, H., McKinstry, W.E., "Analytical Methods for Coal and Coal Products, Vol. I" (C. Karr, Jr., ed.), p.557-568, Academic Press, New York, 1978

fractions within a short time, and did not necessarily intend to identify individual compounds in those fractions.

The results of solvent fractionation using the modified method are summarized in Table 6.3.

6.2.3. Effect of Pyrolysis Temperature

The results of solvent fractionation of tars from the previous study on temperature effect are illustrated in Figure 6.2.

The results in Figure 6.2 indicate that asphaltene yields increased as the temperature increased. It is also indicated that the oil fraction has its maximum yield at 651°C. As described previously, the tar yield itself had its maximum at the same temperature. This fact suggests that the increasing tar yield at 651°C was caused by the increase in the oil fraction yield. On the other hand, the yield of oil fraction at 712°C is lower than that obtained at 651°C, which may imply that, at higher temperature over 700°C, the oil fraction is decomposed in secondary reactions largely producing gaseous products. Consequently only a small amount of the oil fraction was converted to the polymerized compounds, such as the asphaltene and preasphaltene fractions.

In contrast to the asphaltene fractions, which increase with temperature, preasphaltene fractions are almost unchanged over the temperature range between 615°C and 712°C.

Table 6.3. Solvent fractionatrion of tars (summary)

(1) Pentane soluble fraction = oil
(2) Toluene soluble fraction = asphaltene
(3) Methanol soluble fraction = preasphaltene
(4) Methanol insoluble fraction = Preasphaltene

			wt % maf coal				
Run	Coal	T(°C)	(1)	(2)	(3)	(4)	Total
P-70	#2	649	4.95	7.05	2.43	2.88	17.31
P-71	#2	651	5.01	7.25	1.37	1.47	15.10
P-72	#2	555	1.40	3.03	1.10	0.66	6.19
P-74	#2	712	3.36	7.75	1.52	1.41	14.04
P-75	#2L	615	3.73	6.12	2.07	0.89	12.81
P-76	#2L	651	4.56	5.70	1.72	1.28	13.26
P-77	#2L	648	2.98	5.93	1.42	0.88	11.21
P-78	#2L	656	3.79	6.91	1.24	1.42	13.36
P-79	#2L	653	3.96	6.92	2.03	0.68	13.59
P-80	#3	652	4.09	8.47	2.69	2.07	17.32
P-82	A	652	4.60	10.88	2.89	1.57	19.95
P-83	A	732	4.08	10.18	1.83	1.43	17.53
P-84	A	553	3.57	8.70	2.25	0.69	15.20
P-85	#3	581	4.10	7.82	0.93	1.02	13.87
P-86	F	651	4.93	10.29	0.80	1.19	17.21
P-87	F	582	5.97	7.12	0.90	0.67	14.66
			(5.92)	(7.17)	(0.91)	(0.66)	(14.66)

Notes: #2 =Coronach lignite #2
#2L =Coronach lignite #2(low moisture)
#3 =Coronach lignite #3
A =Acid washed Coronach lignite #3
F =Forestburg subbituminous coal
( ) =Repeated test for reproducibility

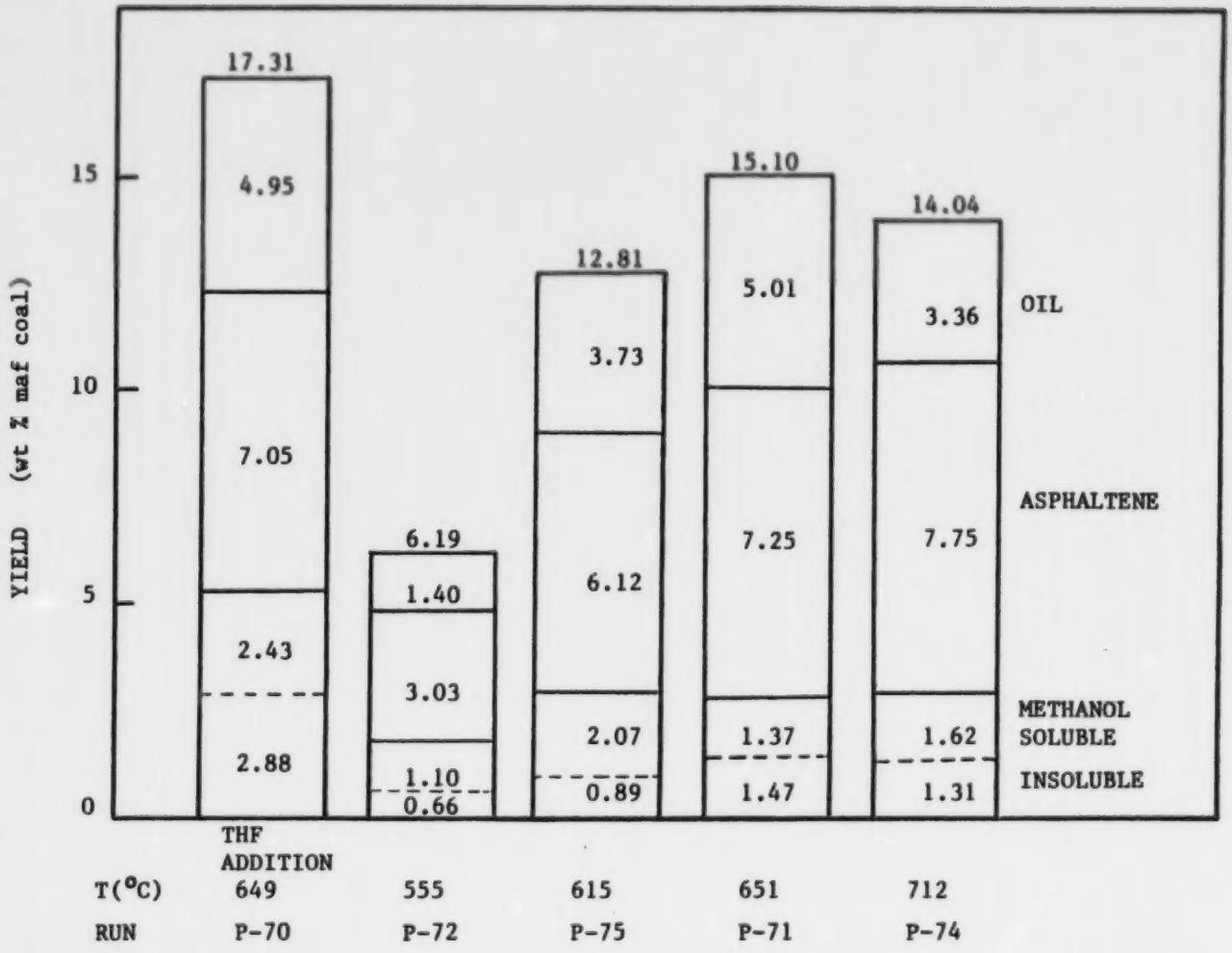


Fig.6.2. Solvent fractionation of tars, pilot plant pyrolysis, Coronach lignite #2, temperature effect.

However, when adding THF in the top of the reactor, the preasphaltene yield markedly increased (5.31% vs. 2.84 wt% maf coal). This increase in the preasphaltene fraction is caused by the increase in both methanol soluble and insoluble fractions. It is interesting to note that the ratio of methanol soluble to insoluble fraction, in fact, does not change in the both cases with and without THF addition.

Judging from the fact that the yields of oil and asphaltene fractions from the both runs done at about 650°C have a close resemblance regardless of THF addition, the increase in the tar yield of Run P-70 with THF addition can be attributed to the increase in the preasphaltene fraction, which consists of the methanol soluble and insoluble fractions.

6.2.4 Effect of Feed Rate

The results of solvent fractionation of tars from the study on feed rate effect are given in Figure 6.3.

From Figure 6.3, it is indicated that oil yields are proportional to tar yields and that methanol insoluble yields are also proportional to tar yields. Asphaltene yields and methanol soluble yields present no significant tendencies either in the order of tar yields or in the order of feed rates.

As shown in the previous section, asphaltene yields increased as the temperature increased. When reasoning by the analogy of

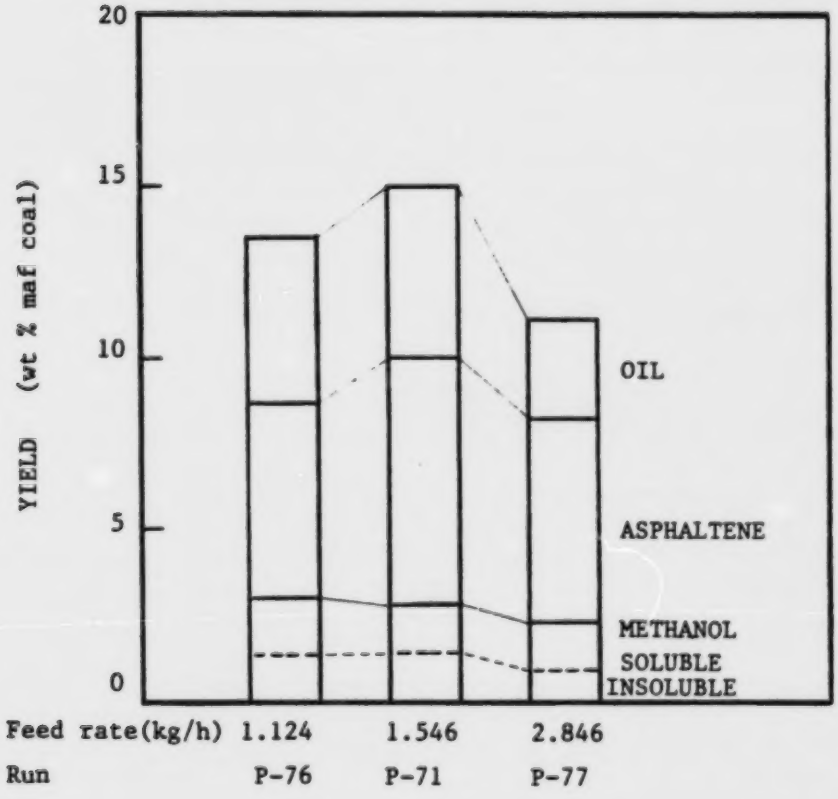


Fig.6.3. Solvent fractionation of tars, feed rate effect, pilot plant pyrolysis, Coronach lignite #2.

this temperature effect, the decrease of asphaltene fractions in both higher and lower feed rate cases corresponds to the decrease of reactor temperature and more precisely asphaltene yields of 5.70 wt% in Run P-76 and 5.93 wt% in Run P-77 are equivalent to a reactor temperature below 615°C.

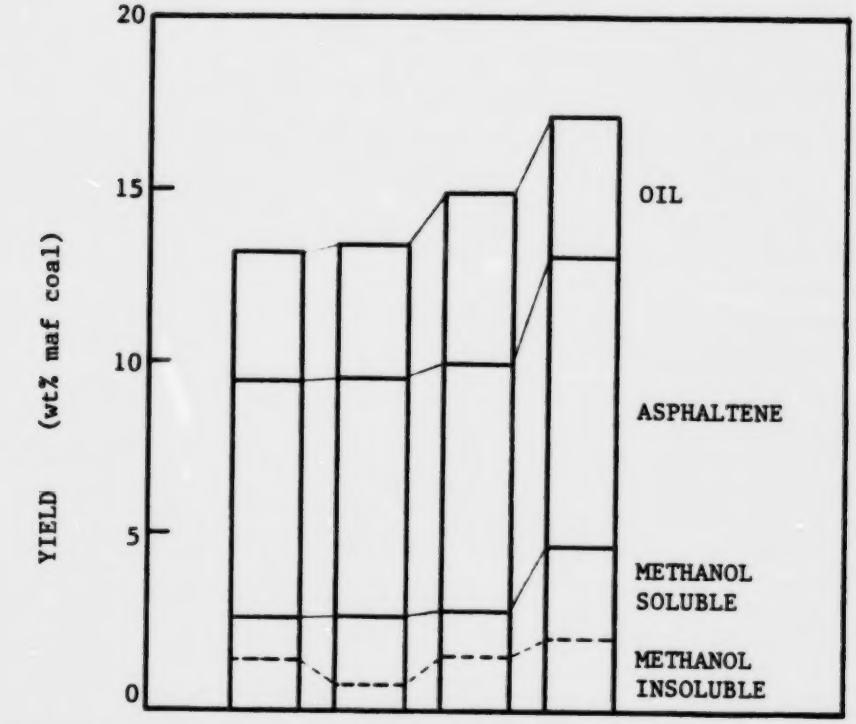
The yields of solvent fractionation in the case of the higher feed rate of 2.846 kg/h at 651°C coincides with the yields in a temperature between 555°C and 615°C. This may imply that, under these two different pyrolysis conditions, coal particles could be thermally decomposed in a similar reaction mechanism, possibly due to a similar particle time-temperature history.

6.2.5 Effect of Residence Time and Moisture

Run P-78 was performed under a short residence time of 0.35 seconds. Runs P-71, P-79 and P-80 were carried out under normal residence times ranging from 0.44 to 0.47 seconds. In these three pyrolysis experiments, three coals of different moisture content were used to investigate the influence of natural moisture present in the original coals.

The results of solvent fractionation of tars from Runs P-71, P-78, P-79, and P-80 are given in Figure 6.4.

In the results of solvent fractionation of tars from Runs P-78 and P-79 shown in Figure 6.4, it can be seen that these two runs of different residence times are very similar in the yields



Moisture(wt%)	2.77	2.77	9.59	22.77
Res.time(s)	0.35	0.44	0.47	0.45
Run	P-78	P-79	P-71	P-80

Fig. 6.4. Solvent fractionation of tars, effect of residence time and natural moisture in coal, pilot plant pyrolysis, Coronach lignite #2.

of oil, asphaltene, and preasphaltene fractions except for different methanol fraction yields. This suggests that the effect of residence time ranging between 0.35s and 0.44s is less significant in terms of the fractionation yields of tars.

It is noteworthy that Run P-80 using the highest moisture content coal gives a higher yield in the asphaltene fraction and on the contrary, Run P-79 performed with the lowest moisture content coal gives a lower yield in the same fraction. It is also observed that the methanol insoluble fractions increase with moisture contents in coals.

While oil yields appear to present no significant tendencies in the order of tar yields, asphaltene yields and preasphaltene yields are proportional to tar yields. These results suggest that tars from these different moisture content coals were produced through different reaction mechanisms even under almost the same operating conditions. This evidence again confirms that there is a possibility that the moisture content in coal participates in the tar producing process of coal pyrolysis.

6.2.6 Effect of Acid Washing

The results of solvent fractionation of tars from Runs P-80, P-82, P-83, P-84, and P-85 are illustrated in Figure 6.5.

From the results shown in Figure 6.5, it is indicated that the methanol insoluble fractions of the preasphaltenes from acid

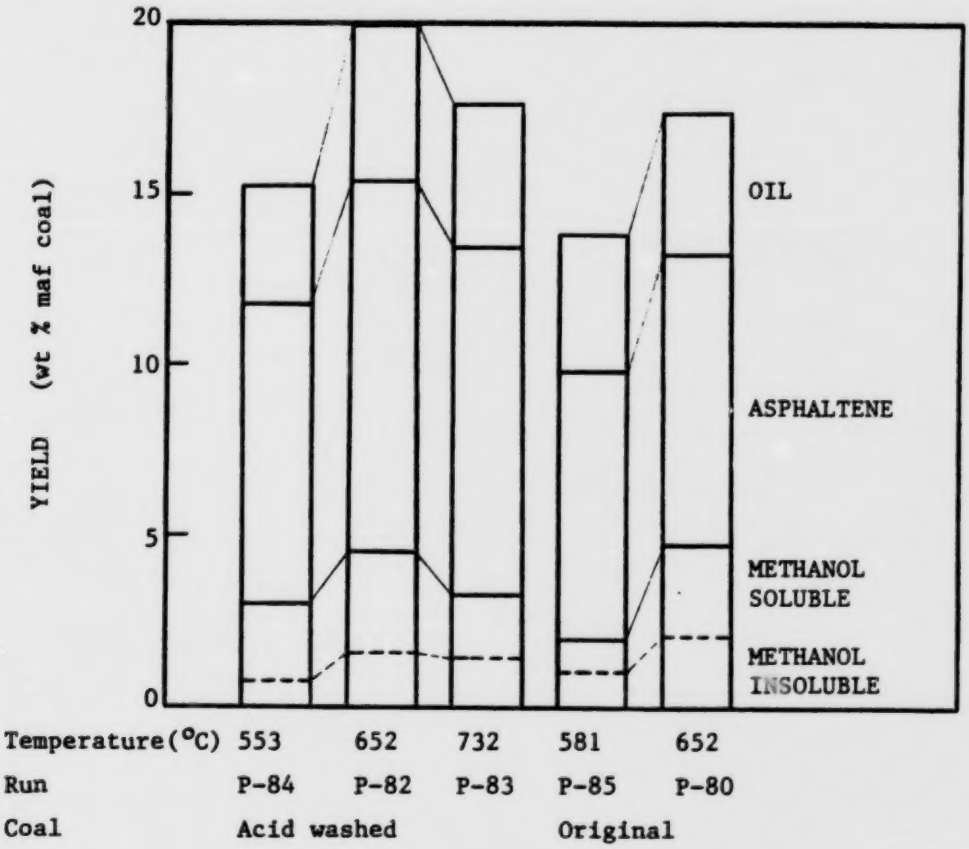


Fig.6.5. Solvent fractionation of tars, effect of acid washing, pilot plant pyrolysis, Coronach lignite #3.

washed Coronach lignite #3 are lower in their yields than those of raw Coronach lignite #3. The methanol insoluble fractions are black agglomerates in appearance. Hence it is likely that these methanol insoluble fractions consisting of polymer-like matter could be formed by the direct decomposition of coal and/or by the repolymerization of highly reactive volatile fragments. Generally, these polymerized compounds are undesirable in practical use, since they potentially cause some difficulty in supplying tar using the prevailing facilities such as pipelines. From this point of view, it is indicated that the acid washing of Coronach lignite #3 might be effective in reducing the methanol insoluble fractions comprising polymer-like components.

Although Runs P-83 and P-80 give almost the same tar yields, the results of solvent fractionation are quite different, namely the yield of the asphaltene fraction of P-83 with acid washed Coronach lignite #3 is much higher than that of P-80 with raw Coronach lignite #3. Even the asphaltene fraction of P-84 operated at the lowest temperature of 553°C is slightly higher than that of P-80.

From these observations it is suggested that the acid washed Coronach lignite #3 always gives higher asphaltene yields than the raw lignite at temperatures tested.

On the other hand, the oil and preasphaltene yields of Runs P-80 and P-85 appear to present virtually no significant trend when compared with those of Runs P-82 and P-84.

Consequently, it can be concluded that the increased tar yields by acid washing treatment are primarily due to the increase in the yields of asphaltene fractions.

6.2.7 Forestburg Subbituminous Coal Tar

The results of solvent fractionation of tars obtained with Forestburg subbituminous coal are illustrated in Figure 6.6, together with the results of Coronach lignite #3.

A repeated test of solvent fractionation of tar obtained at 582°C with Forestburg subbituminous coal indicated that the maximum difference between duplicate results was 0.05 wt% maf coal (0.38 wt% tar). This reproducibility indicates a small experimental error.

A comparison between results of solvent fractionation shown in Figure 6.6 indicates that preasphaltene fractions of Forestburg subbituminous coal are much lower than those of Coronach lignite #3, in particular at about 650°C. The decrease in the preasphaltene fraction at 651°C with Forestburg subbituminous coal is almost quantitatively offset by higher yields of oil and asphaltene fractions as compared to data with Coronach lignite #3 at 652°C.

At about 580°C, however, one rather unexpected result was obtained with Forestburg subbituminous coal, namely a somewhat higher oil yield was observed at this low temperature and this

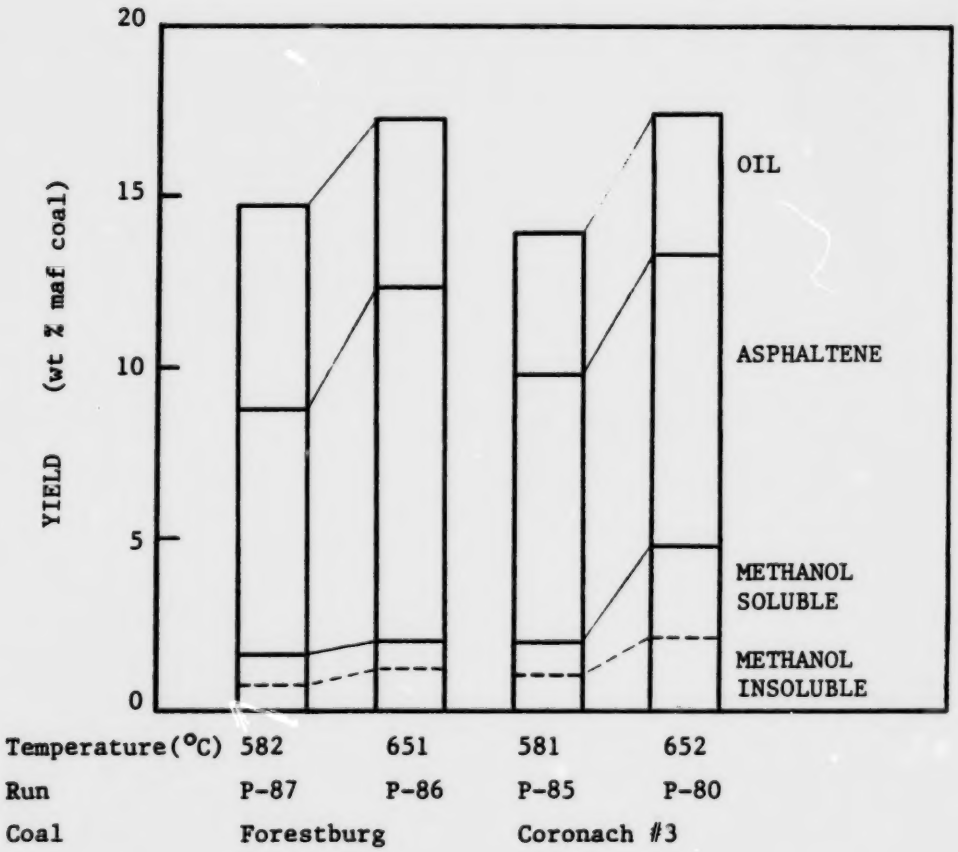


Fig.6.6. Solvent fractionation of tars, comparison between Forestburg subbituminous coal and Coronach lignite #3, pilot plant pyrolysis.

result was reproducible to 0.05% maf coal (0.38 wt% tar) as mentioned above.

Figure 6.6 clearly shows the apparently greater oil formation behaviour with Forestburg subbituminous coal as compared with the Coronach lignite #3.

It should also be noted that Forestburg subbituminous coal and acid washed Coronach lignite #3 shown in Figure 6.5 have similar yields of oil and asphaltene fractions at about 650°C, but different yields of those fractions at temperature below 600°C.

It is difficult to postulate an explanation for the similarities and differences in behaviour of Forestburg subbituminous coal and acid washed Coronach lignite #3. One similarity which should be noted is that both Forestburg subbituminous coal and acid washed Coronach lignite #3 have almost the same ash content. One of the chief differences between them is that lignites are, in general, more porous or open-structured than subbituminous coals.

6.3 Identification of Compounds

6.3.1 Preliminary Experiments

A toluene soluble fraction of tar was analyzed by GC/MS. The tar sample used was P-77 tar obtained from Coronach lignite #2 and subjected to solvent fractionation.

A small portion of toluene soluble fraction was sampled prior to the fractionating operation using a Soxhlet extractor. This sample was stored in a refrigerator to avoid further spontaneous polymerization and condensation reactions induced by heat or by light or by both of them.

The sample was kept in a glass vial during storage, because some reactive compounds containing oxygenated functional groups are prone to polymerize on contact with metals such as iron.

Conditions used for GC/MS analysis are summarized in Table 6.4.

A sample of 0.2 l of toluene soluble fraction was chromatographed on a 12m x 0.22mm i.d. fused quartz capillary column coated with cross-linked methyl silicone as a stationary phase. The column was temperature programmed from 120°C to 250°C at a rate of 10°C/min and was directly coupled to a Hewlett-Packard 5970 mass selective detector. Detailed GC/MS data, such as scan acquisiton conditions, total ion chromatograms and library search results, can be found as Appendices C, D, and E, respectively in the MASc thesis of S. Miyawaki (18).

Twenty six compounds gave distinguishable peaks in a total ion chromatogram. Fourteen of these compounds were identified using the National Bureau of Standards data bank, ten of them with a match quality of more than 95% and four of them with more than 90%.

Table 6.4. Conditions of GC/MS analysis

Instrument(GC)	Hewlett-Packard 5890	
Column	Cross-linked methyl silicone 12m x 0.22mm i.d. Film thickness 0.33μm	
Detector(MS)	Hewlett-Packard 5970 mass selective detector	
Workstation	Hewlett-Packard 9133 with NBS data bank	
Injection temp.	290°C	
Carrier gas	He at 56 ml/min	
Temperature programme		
	Initial	120°C
	120-250°C	rate 10°C/min
	250°C	for 17min
Samples	Toluene soluble fraction in toluene	0.2μl
	Pentane soluble fraction in pentane	0.2μl
	Aqueous liquor*	0.5μl

Note: * Temperature programme was terminated in 5 min at 170°C due to absence of relevant compounds.

The identified compounds are shown in Figure 6.7.

From the results shown in Figure 6.7, it is clearly visible that the toluene soluble fraction of tar consists primarily of phenol derivatives (phenol, cresols, xylenol, and ethyl phenol) and benzenediol derivatives (catechols and resorcinol).

A pentane soluble fraction from Run P-77, the toluene soluble fraction of which was already analyzed by GC/MS, was subjected to detailed compositional analysis by GC/MS.

Conditions of GC/MS were the same as those employed for analysis of the toluene soluble fraction, as previously shown in Table 6.4.

The GC/MS total ion chromatogram of the pentane soluble fraction obtained from P-77 tar is shown in Figure 6.8, together with that of 1-eicosene used as a calibration compound for alkenes. It is clear from Figure 6.8 that the pentane soluble fraction contains appreciable amounts of paraffinic alkanes and/or alkenes, which, as a rule, appear on the chromatogram at regular retention-time intervals.

Detailed chromatograms are given in Figures 6.9 and 6.10.

The identification of individual compounds shown in Figure 6.9 indicates that the pentane soluble fraction contains : phenol, o-cresol, m/p-cresol, xylenol and ethyl phenol, which were all found in the toluene soluble fraction reported previously.

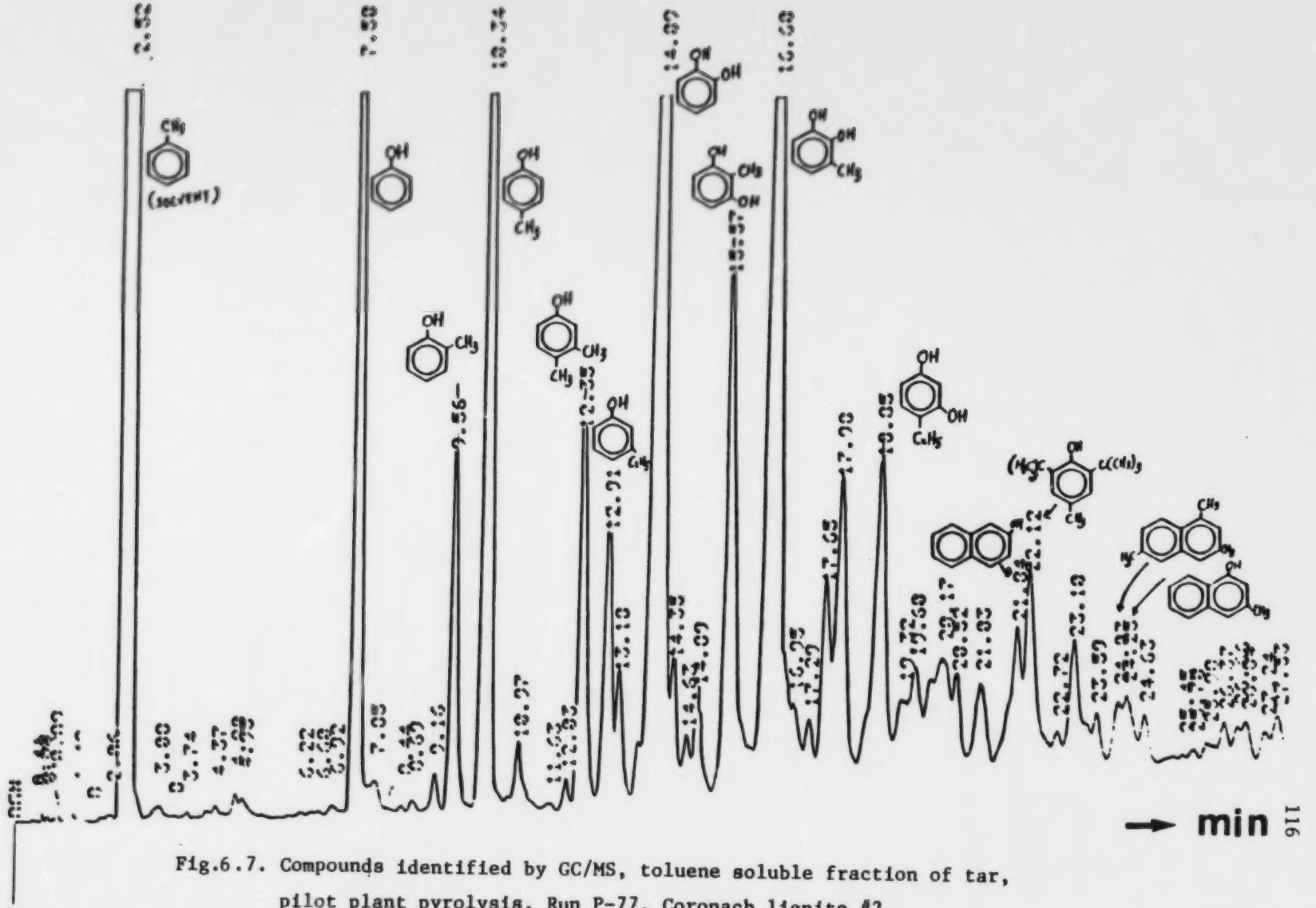


Fig.6.7. Compounds identified by GC/MS, toluene soluble fraction of tar, pilot plant pyrolysis, Run P-77, Coronach lignite #2.

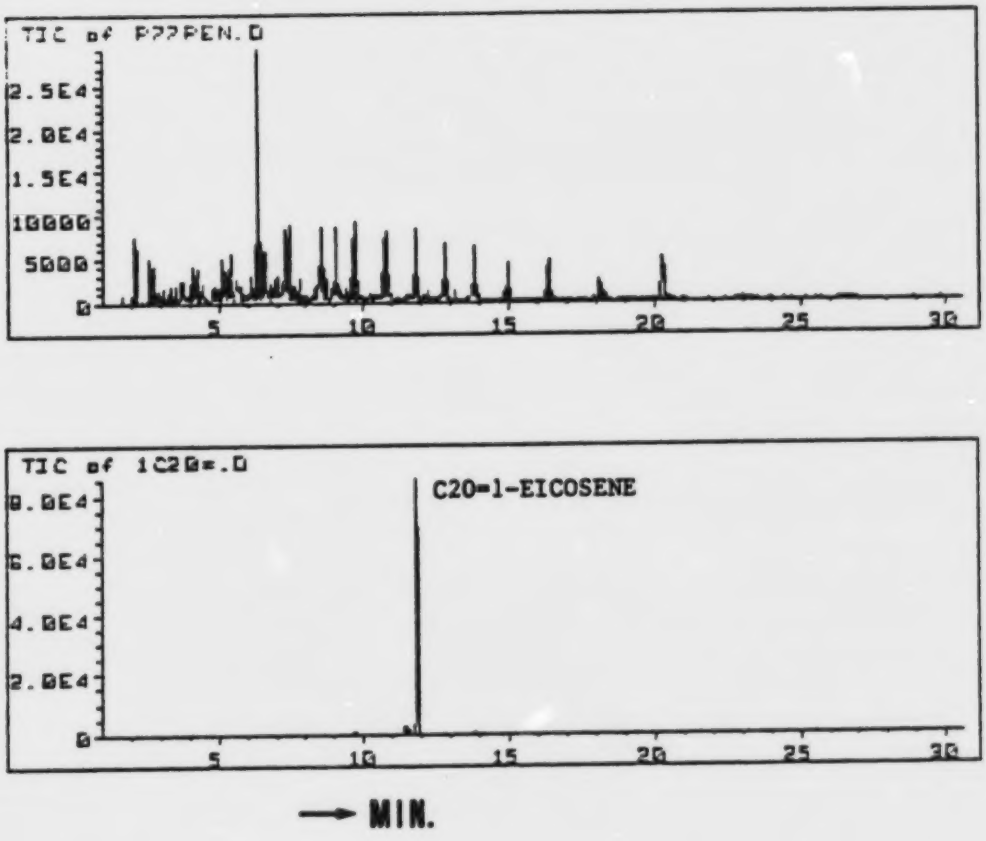
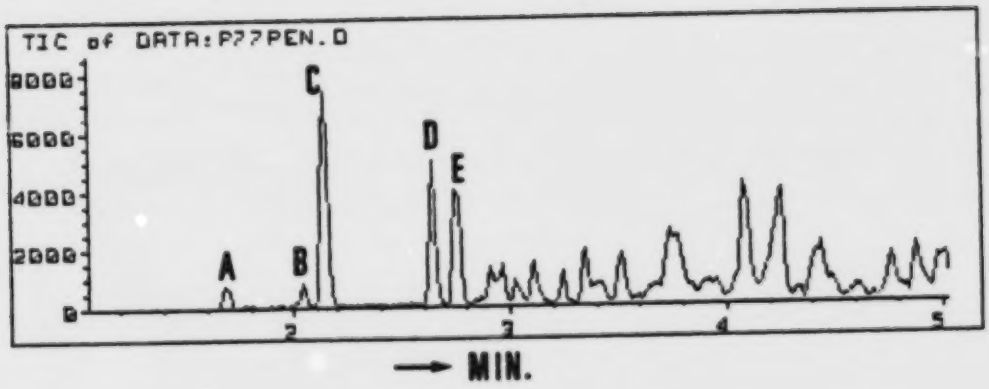


Fig. 6.8. Total ion chromatogram of pentane soluble fraction, pilot plant pyrolysis, Coronach lignite #2, Run P-77.



A: PHENOL

B: o-CRESOL

C: m-/p-CRESOL

D: XYLENOL

E: ETHYL PHENOL

Fig. 6.9. GC/MS analysis of low boiling compounds in pentane soluble fraction, Coronach lignite #2, Run P-77.

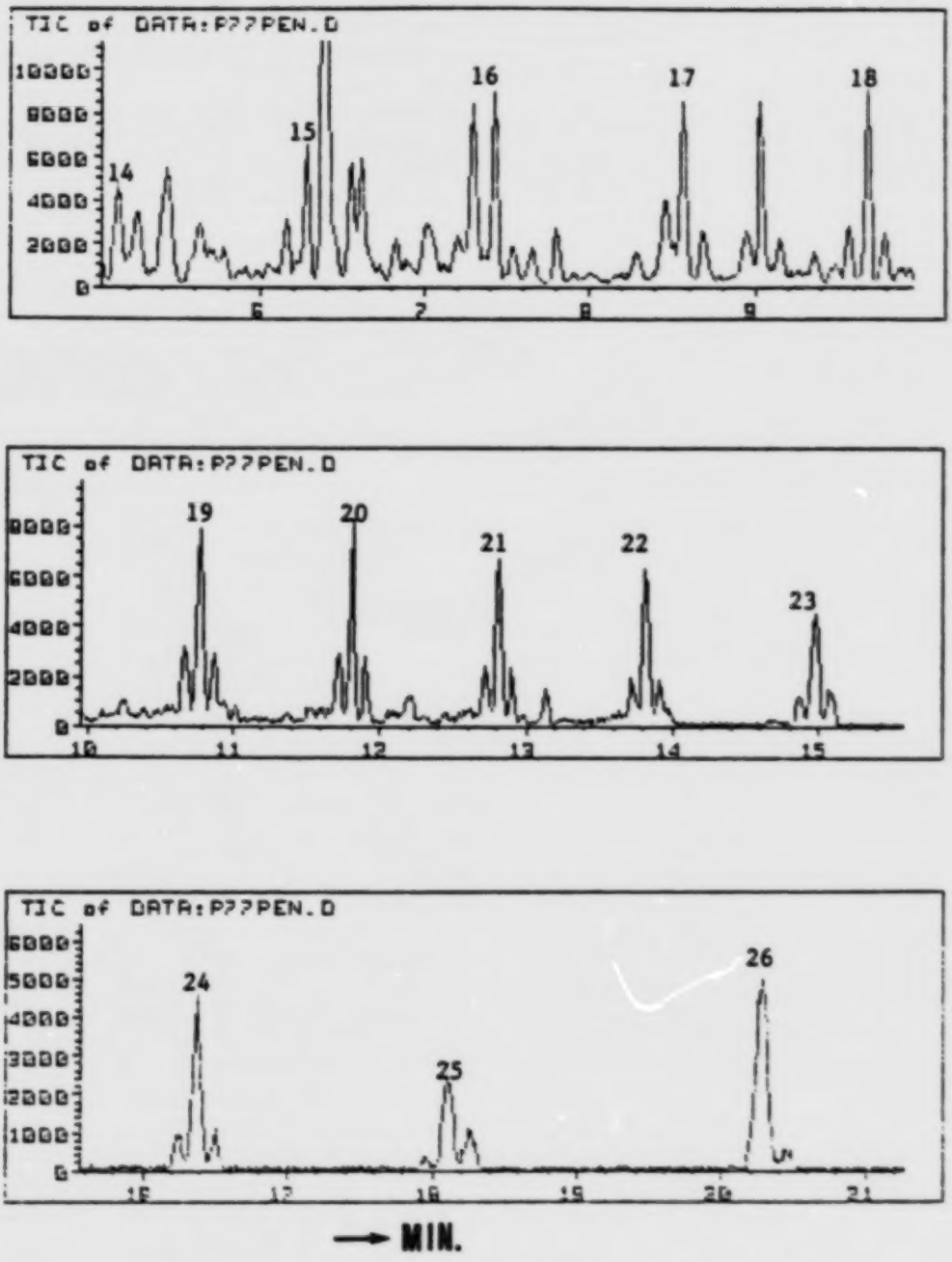


Fig.6.10. GC/MS analysis of alkenes in pentane soluble fraction, pilot plant pyrolysis, Coronach lignite #2, Run P-77.

Note: Pertinent peaks are labeled with numbers corresponding to the carbon atoms of alkanes.

Figure 6.10 clearly demonstrates the presence of C_{14} to C_{26} alkenes, and relatively small amounts of n-alkanes, which appear at the right side of the alkenes.

An interesting feature is also shown in alkene/n-alkane pairs, namely that a third distinct peak is observed at the left side of each alkene/n-alkane pair. Even though their exact molecular structure has not been completely elucidated, the position of the peaks on the chromatogram appears to be equivalent to structural isomers of the alkenes or n-alkanes.

From these data it can be concluded that the pentane soluble fraction contains considerable amounts of phenol derivatives, alkenes and alkanes. The results of the identification of major compounds are in good agreement with data on a low temperature coal tar reported by Evans et al. (19), which were obtained using gel permeation chromatography (GPC). It was suggested by Evans et al. that GPC may offer possibilities for fractionating coal liquids according to chemical type in addition to the normal separation on the basis of molecular size and thus can be further used for determination of the nature of coal-derived tars in place of the time-consuming solvent fractionation methods currently used.

The most distinctive feature of these low temperature pyrolysis oils is the presence of large proportions of straight-chain alkenes. The presence of olefins in the pyrolysis oils is not

unexpected because during pyrolysis radical species are formed that can undergo α-bond cleavage to yield olefins. When the α-CH bond is broken (equation 6.1), alkenes are formed that can decompose by β-C-C bond cleavage and hydrogen transfer to yield ethylene.

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH_2 + H_2 \qquad (6.1)$$

$$R\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH_2 \longrightarrow R\text{-}CH{=}CH_2 + CH_2{=}CH_2 \qquad (6.2)$$

It is well known that ethylene is an important component of the gaseous products resulting from pyrolysis of coal.

According to the study on the chemical structure of distillates obtained from pyrolysis of Australian (Liddell) bituminous coal [Collin, Gilbert, Philp and Wilson (20)], the pyrolysis oil from high rank coals also contained considerable proportions of benzene derivatives, methyl naphthalenes, and tetralin. The presence of these compounds was not observed in the present study with Coronach lignite.

6.3.2 Composition of Toluene Soluble Fractions

The preliminary identification of the prominent components present in the toluene soluble fraction of P-77 tar was reported previously.

With the same method used with P-77 tar, toluene soluble fractions of original and acid washed Coronach lignite tars and Forestburg subbituminous coal tars were analyzed by high resolution gas chromatography.

Eight major compounds, namely, phenol, o-cresol, m/p-cresol, xylenol, ethyl phenol, catechol, methyl resorcinol, and methyl catechol were selected and semi-quantitatively determined by a flame ionization detector.

Conditions of gas-chromatographic separation were given previously. A representative calibration curve for toluene is also shown in Figure 6.11. The chromatograms for the toluene soluble fractions of the various tars are shown in Figures 6.12 to 6.18. The results for the eight major components selected are summarized in Table 6.6.

Table 6.6 indicates that the concentrations of catechol and its derivative increase considerably when pyrolyzing the acid washed Coronach lignite, while the concentrations of phenol and its derivatives are comparatively unaffected by the acid washing treatment. This fact suggests that the reactive surface of the acid washed coal favourably affects the evolution of catechol and its derivative presumably through a different reaction mechanism in the thermal decomposition at about 650°C. The original Coronach lignite #3 might be assumed to be pyrolyzed via an intermediate mode of decomposition between the acid washed Coronach lignite and Forestburg subbituminous coal if the catechol and its derivative can be assumed not to be involved in secondary vapour-phase reactions at about 650°C.

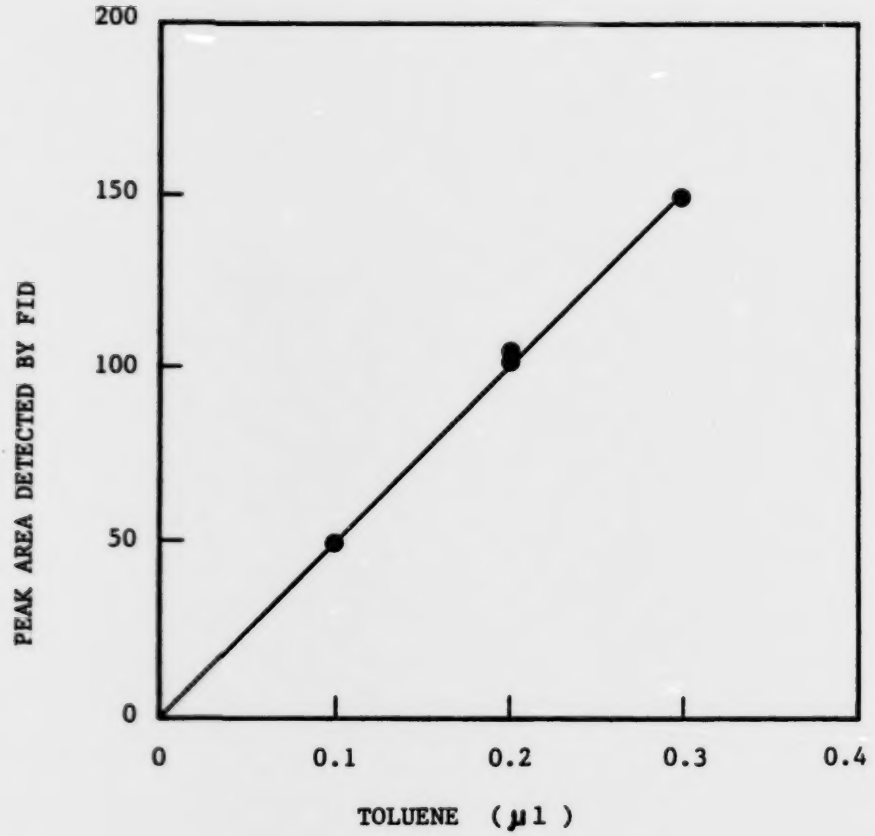
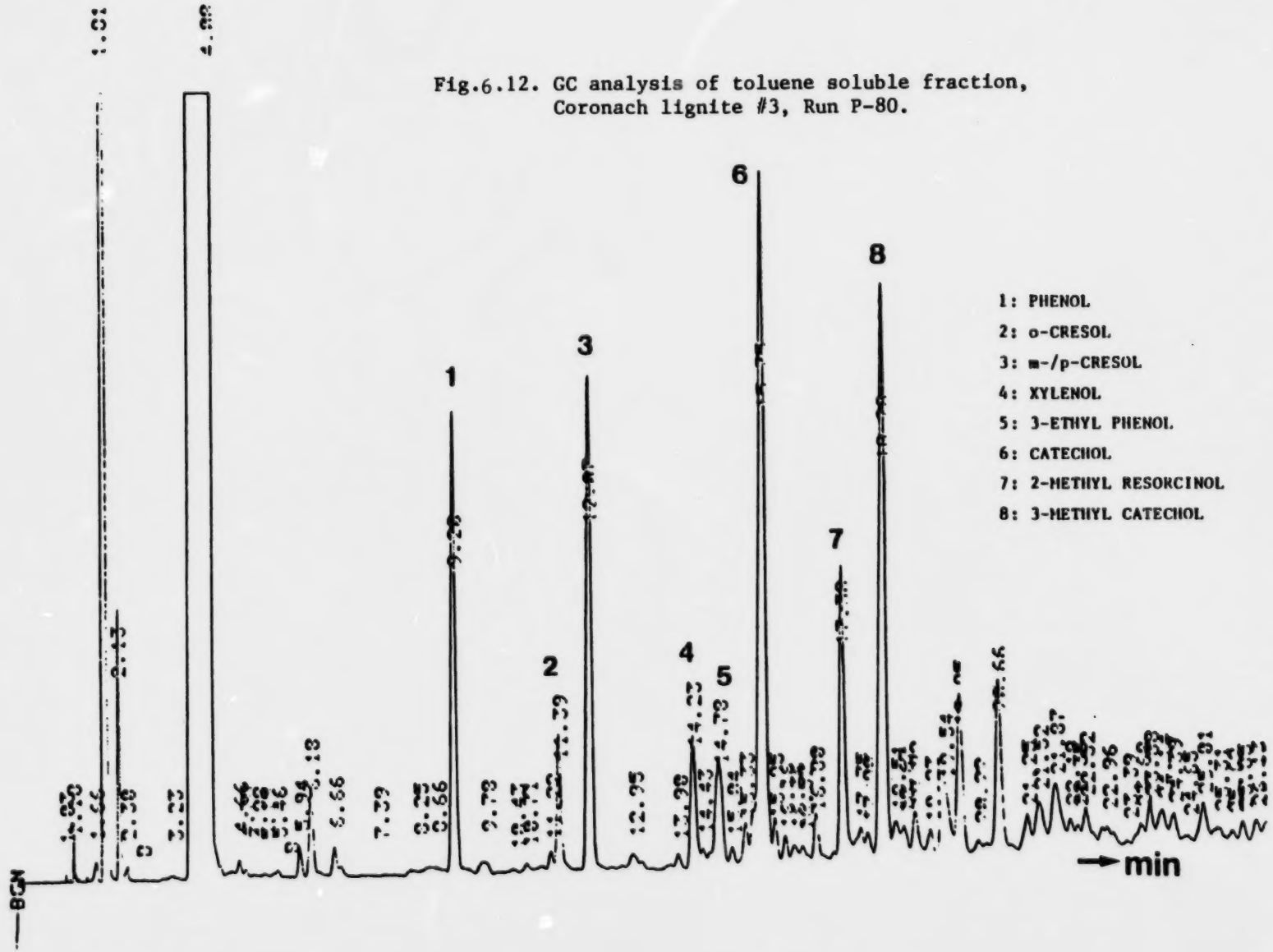


Fig.6.11. Calibration curve for toluene.

Instrument: Perkin-Elmer Sigma 3B
Column: DB-5,30m x 0.5mm o.d.
Detector: FID at 290°C
Carrier gas: N2 at 8 ml/min

Fig.6.12. GC analysis of toluene soluble fraction,
Coronach lignite #3, Run P-80.



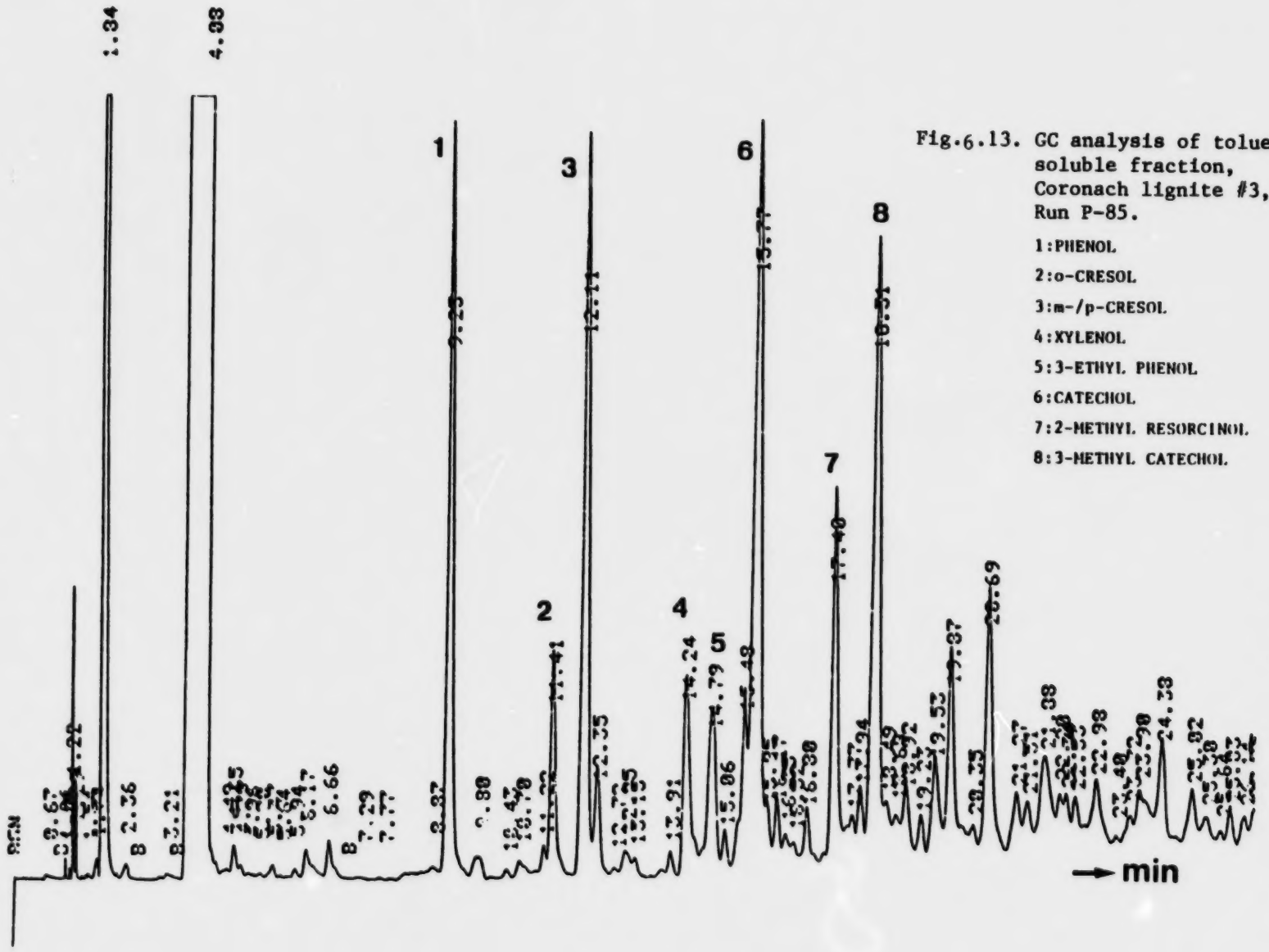


Fig.6.13. GC analysis of toluene soluble fraction, Coronach lignite #3, Run P-85.

1:PHENOL
2:o-CRESOL
3:m-/p-CRESOL
4:XYLENOL
5:3-ETHYL PHENOL
6:CATECHOL
7:2-METHYL RESORCINOL
8:3-METHYL CATECHOL

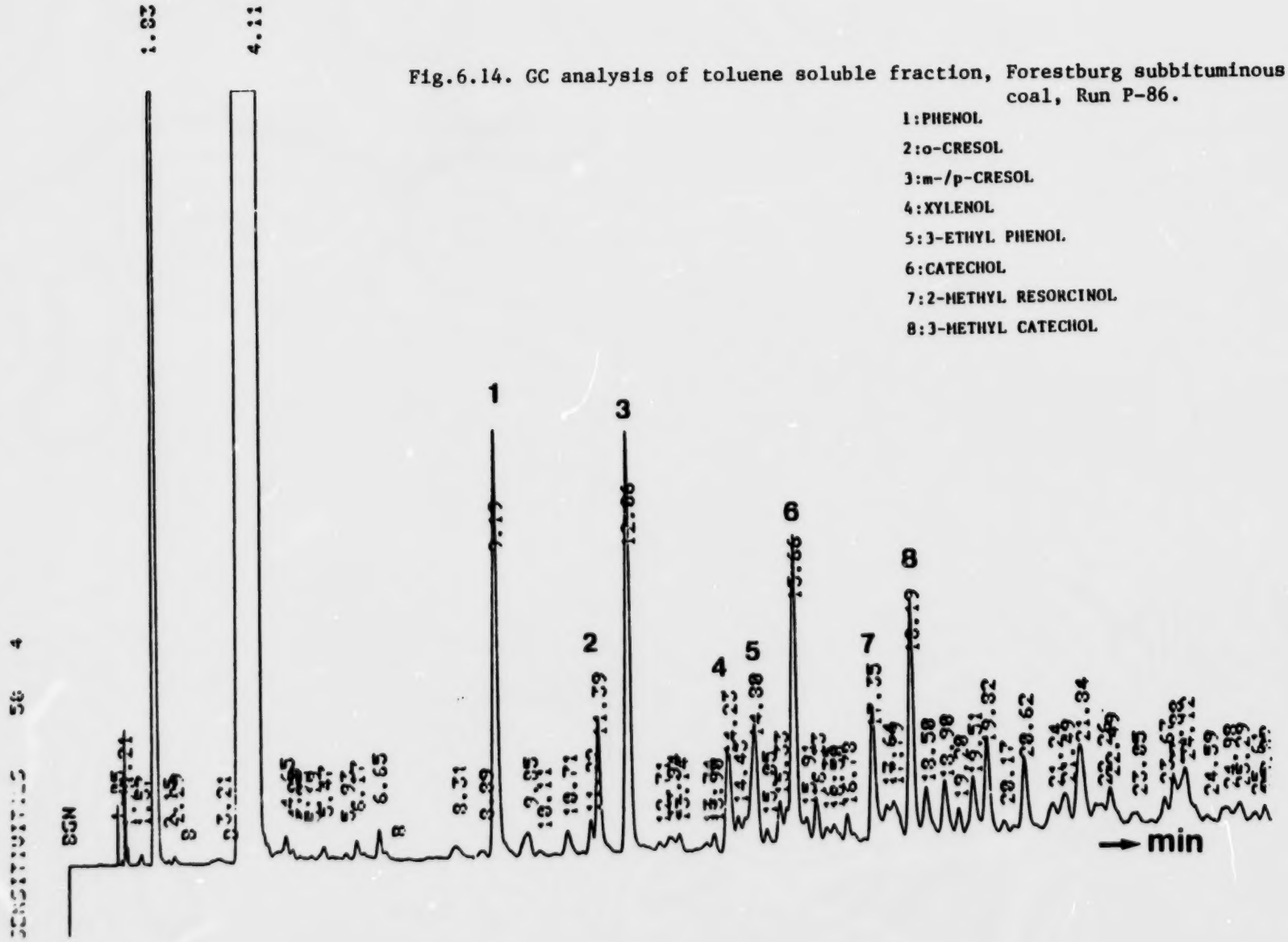


Fig.6.14. GC analysis of toluene soluble fraction, Forestburg subbituminous coal, Run P-86.

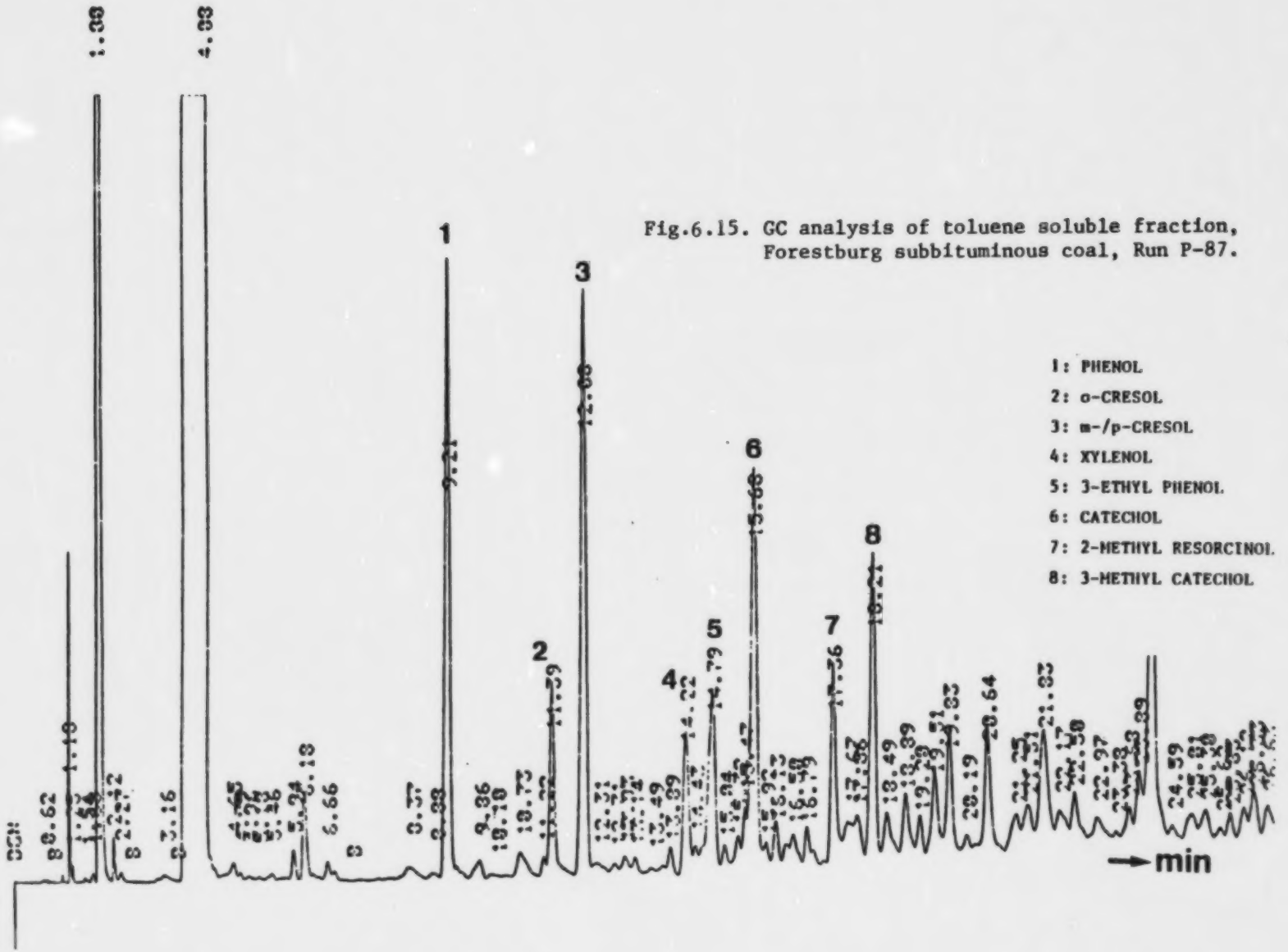


Fig.6.15. GC analysis of toluene soluble fraction, Forestburg subbituminous coal, Run P-87.

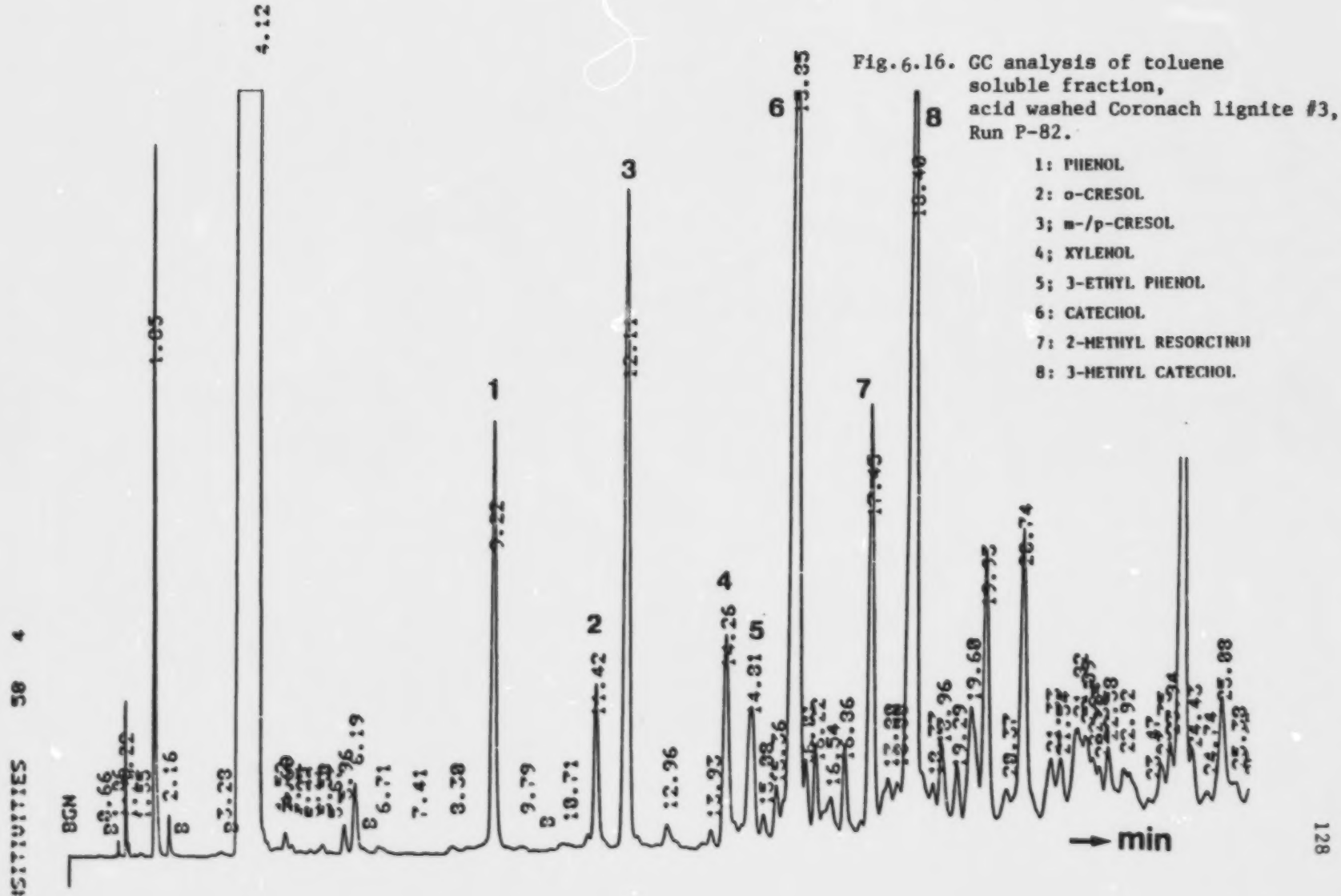


Fig.6.16. GC analysis of toluene soluble fraction, acid washed Coronach lignite #3, Run P-82.

1: PHENOL
2: o-CRESOL
3; m-/p-CRESOL
4; XYLENOL
5; 3-ETHYL PHENOL
6: CATECHOL
7: 2-METHYL RESORCINOL
8: 3-METHYL CATECHOL

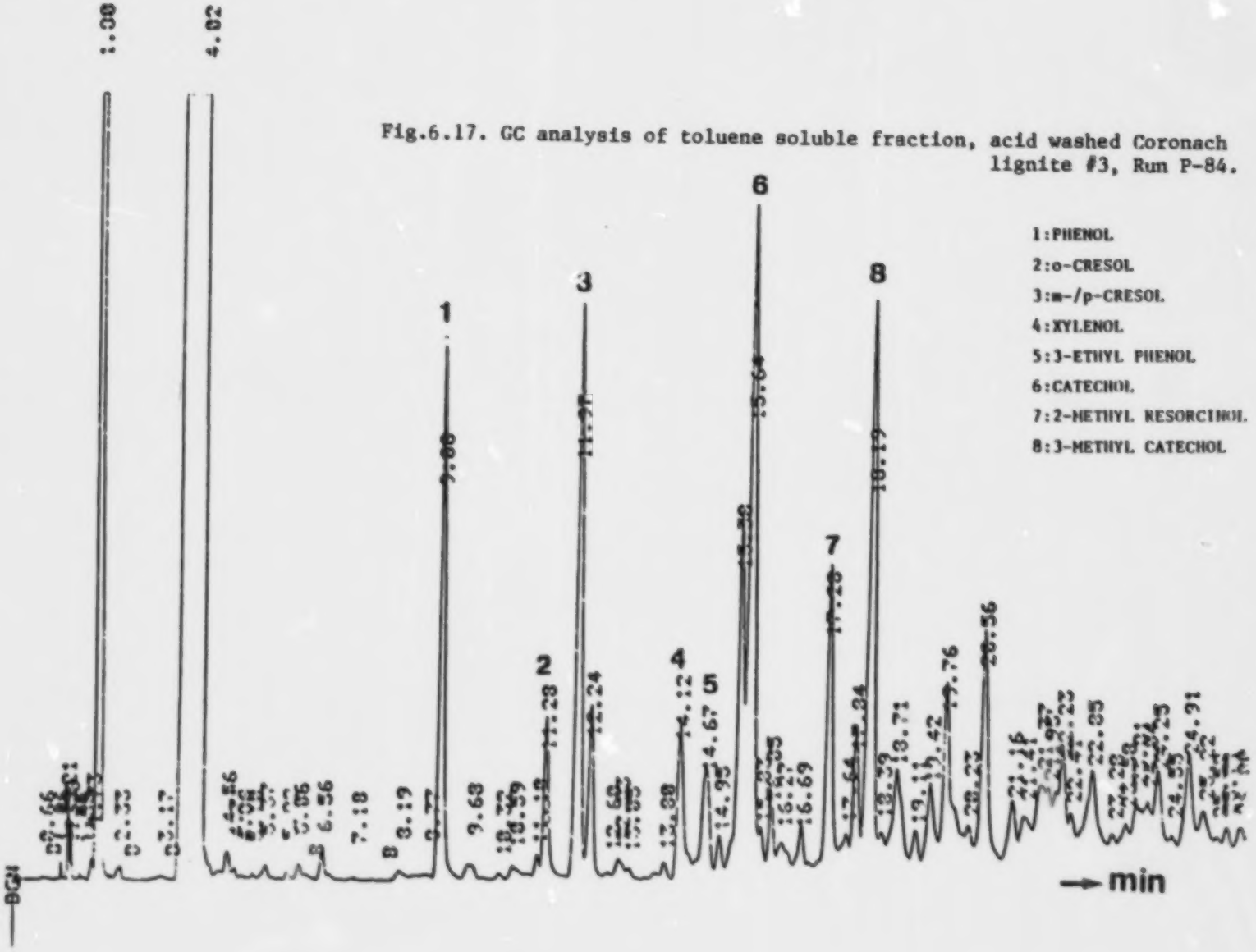


Fig.6.17. GC analysis of toluene soluble fraction, acid washed Coronach lignite #3, Run P-84.

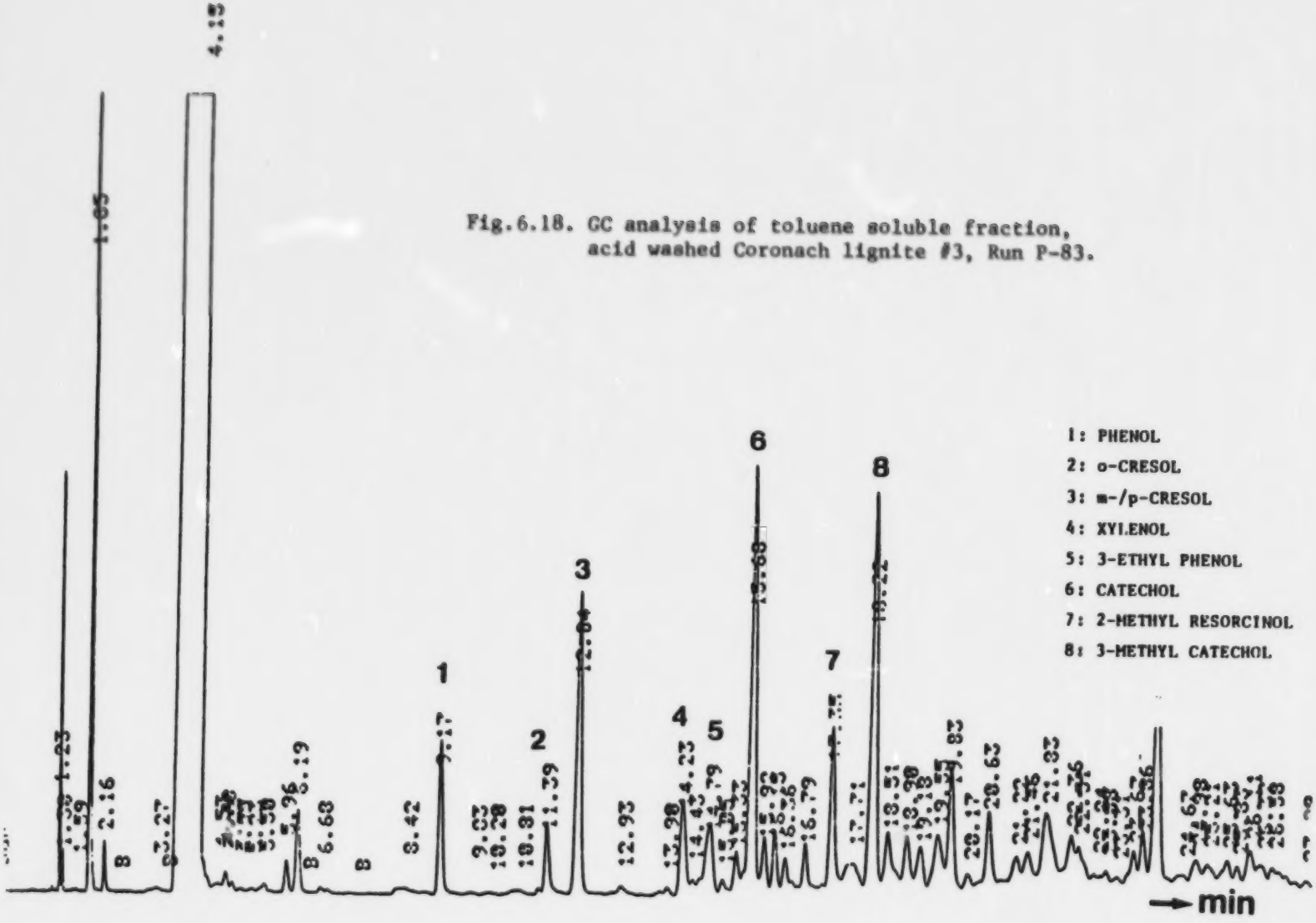


Fig.6.18. GC analysis of toluene soluble fraction, acid washed Coronach lignite #3, Run P-83.

Table 6.6. Corrected peak area of prominent components in toluene soluble fraction of tar, pilot plant pyrolysis, low rank coals.

	Coronach lignite #3					Forestburg subbituminous	
	Original		Acid washed				
Run	P-85	P-80	P-84	P-82	P-83	P-87	P-86
Temp.(°C)	581	652	553	652	732	582	651
Corrected peak area *							
Phenol	2.24	1.17	1.51	1.27	0.39	1.71	1.21
o-Cresol	0.69	0.36	0.49	0.54	0.22	0.55	0.42
m/p-Cresol	2.47	1.47	1.84	2.20	0.90	1.82	1.36
Xylenol	0.81	0.43	0.62	0.84	0.33	0.48	0.38
3-Ethyl phenol	0.81	0.49	0.55	0.74	0.36	0.81	0.63
Catechol	3.31	2.62	2.67	4.58	1.39	1.46	1.15
2-Methyl resorcinol	1.35	0.88	1.09	1.55	0.53	0.65	0.48
3-Methyl catechol	2.69	2.02	2.26	4.39	1.30	1.02	0.77
Total	14.37	9.44	11.03	16.11	5.42	8.50	6.40

Note: * Corrected peak area $= \frac{\text{peak area by FID}}{0.3\mu l - \mu l \text{ of toluene}} \times 0.2\mu l$

Figure 6.19 shows the approximate concentrations of the major compounds as a percentage of maf coal. Whereas tar yields of Coronach lignite #3 and Forestburg subbituminous coal are almost identical in amount as reported previously, the concentrations of individual components, such as catechol and its derivatives, are not necessarily equivalent. This difference in the tar compositions appears to reflect some differences in parental structures of these low rank coals.

As an example, characterization studies of the organic structure and reactions of Northern Great Plains lignites have been reported (2). Their work demonstrated that the aromatic clusters generally contained no more than 1 or 2 aromatic rings. Oxygen containing functional groups were abundant; these coals typically contained 20% oxygen (daf). The principal groups were found to be carboxylic and phenolic. The inorganic constituents occurred in at least three modes. The alkali and alkaline earth elements were present as ion-exchangeable cations associated with carboxylic groups. The principal extraneous minerals were quartz, clays, and pyrite. The unique features of both organic structure and distribution of inorganic species might have significant effects on the chemistry of coal pyrolysis. A consideration of molecular models for coal and precise measurement of individual components by quantitative analysis of tar could provide further indications of the patterns of molecular fragmentation.

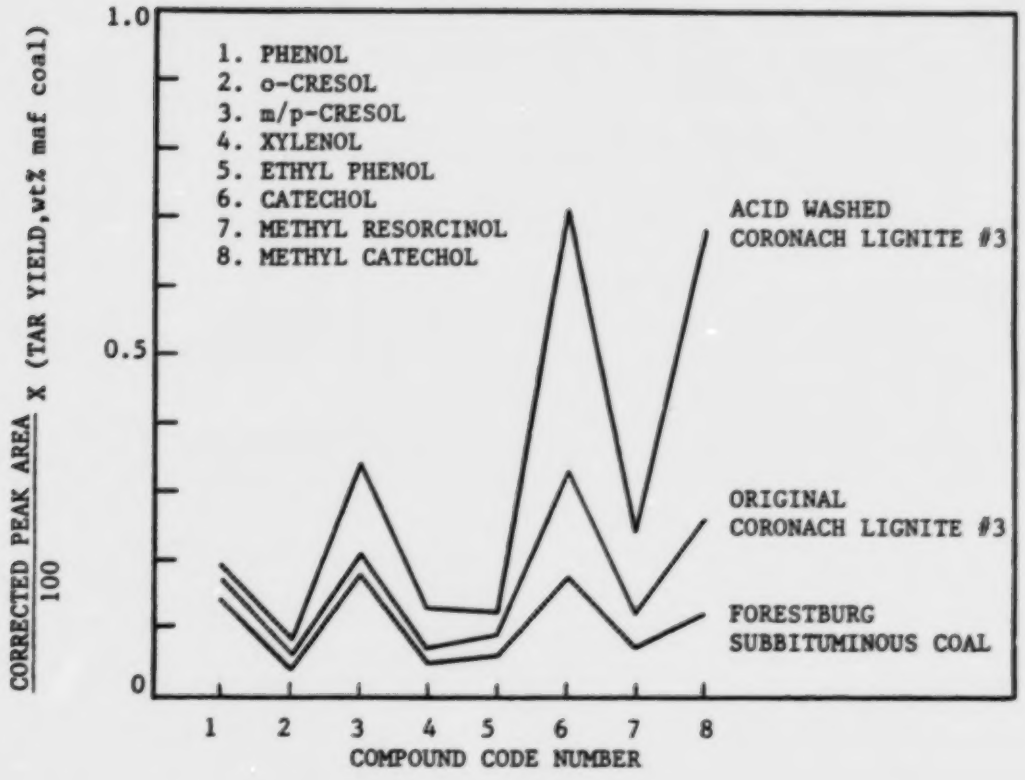


Fig. 6.19. Concentration of major compound in toluene soluble fraction, pilot plant pyrolysis, low rank coal.

Note: Compounds are labeled with numbers 1 to 8 in order of retention time.

6.3.3 Thermogravimetric Analysis of Tar

A thermogravimetric analysis of Coronach tar was performed at a heating rate of 100°C/min. Figure 6.20 gives the thermogram of the tar obtained from Run P-80 with Coronach lignite #3 at 652°C.

As the data given in Figure 6.20 show, although the heating rate is maintained at 100°C/min, the rate of devolatilization obviously decreased with increasing temperature. This decrease in the rate of devolatilization might be ascribed to some thermal alteration of reactions between reactive compounds at these high temperatures.

Table 6.7 shows weight losses in seven temperature intervals. The results shown in Table 6.7 indicate that the maximum rate of devolatilization was attained between 200°C and 300°C. Although temperatures observed in thermogravimetric measurements do not necessarily coincide with normal boiling points of compounds present in tar, it is noteworthy that the normal boiling points of major compounds identified by GC/MS are mainly included in the temperature interval between 200°C and 300°C.

The fraction in the boiling range between 200°C and 300°C generally corresponds to petroleum-originated kerosene and diesel fuel, which occupy very important positions in transportation fuel categories. Those liquid fractions from coals are potentially capable of forming an alternative energy source which would partly

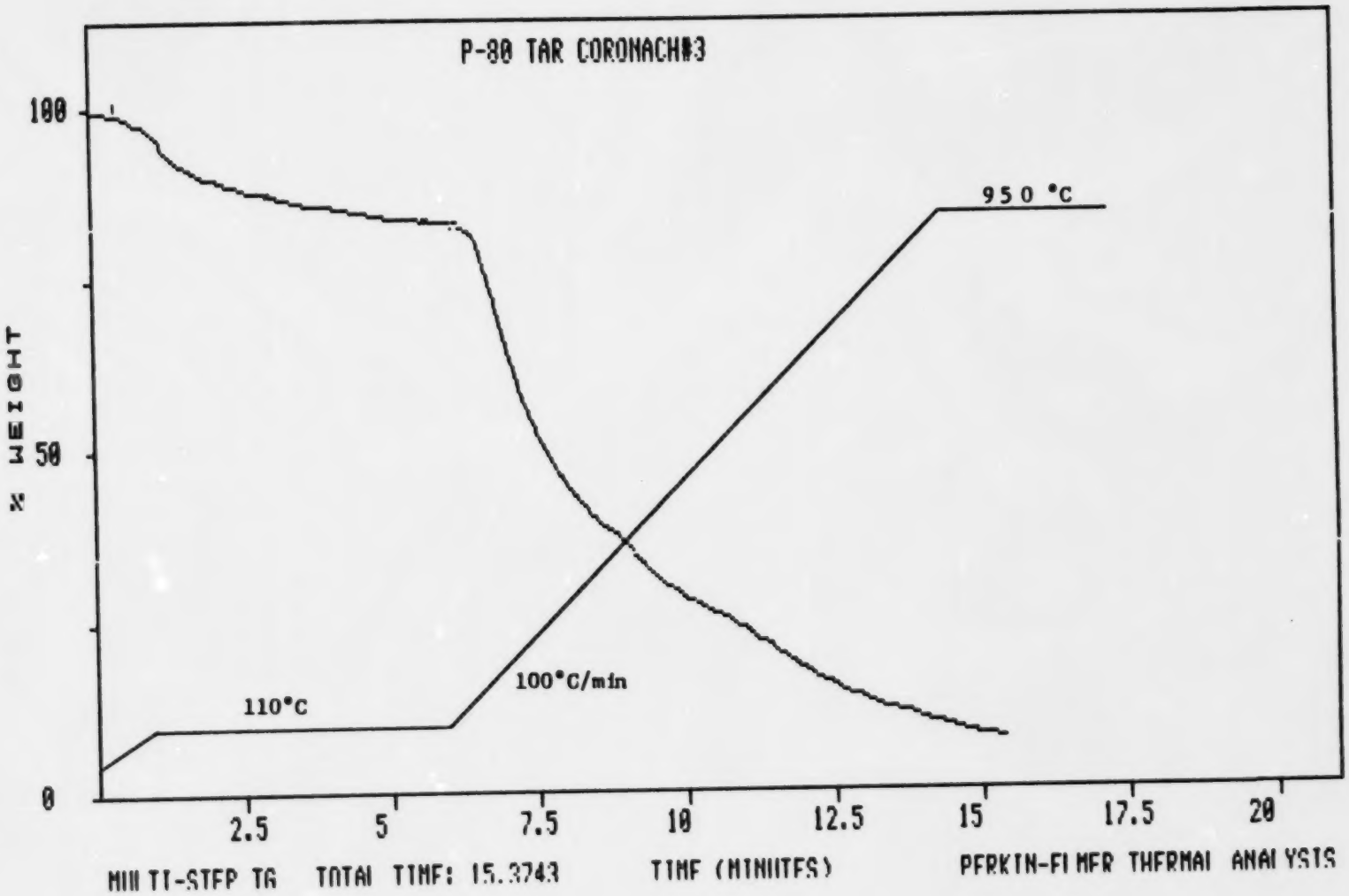


Fig.6.20. Thermogram of tar, pilot plant pyrolysis, Coronach lignite #3, Run P-80.

Table 6.7. Devolatilization of tar measured by TGA in nitrogen, Coronach lignite #3, Run P-80.

Temperature(°C)	wt % tar
50-110	16.8
110-200	12.4
200-300	23.5
300-400	9.7
400-500	8.8
500-600	3.6
600-950	25.2
Total	100.0

Notes: Normal boiling point of major components found in toluene soluble fraction.

-200°C = phenol(182)
o-cresol(191)
-300°C = p-cresol(201.9)
m-cresol(202.2)
3-ethyl phenol(214)
3,4-Xylenol(218)
catechol(246)
3-methyl catechol(241)
2-methyl resorcinol(264)
2-hydroxy naphthalene(295)

compensate for an estimated future deficiency in middle distillates obtainable from crude oils.

Therefore, data on the composition of the fraction in this boiling range might be vital for product quality control, assessment of process parameters and so on in the production of liquid hydrocarbon fuels from coal. Futhermore, comparison of products from coal with conventional petroleum distillates could furnish some useful information on the types of chemical reactions that are important in rapid pyrolysis of coal.

6.4 AQUEOUS LIQUOR

Within the wide limits of variability attributable to different coal compositions, all pyrolysis runs showed that, under otherwise comparable conditions, yields of reaction water are largely determined by competition for hydrogen between carbon and oxygen.

Pyrolytic water yields from low rank coals were in the order: Forestburg subbituminous coal (12.00 % maf coal) > original Coronach lignite #3 (8.50 % maf coal) > acid washed Coronach lignite #3 (7.41 % maf coal) at about 650°C. The tar yields of these coals were in the reverse order. Therefore it is likely that yields of water rise in part at the expense of tar in pyrolysis of these low rank coals.

Analyses of aqueous liquid products obtained from low rank coals were performed in an attempt to clarify the ingredients of

them. The pH values of aqueous liquors obtained from low rank coals are given in Figure 6.21.

The aqueous liquors derived from Forestburg subbituminous coal have pH higher than 7.5 and thus they appear to contain no acidic ingredients. It should be noted, however, that the aqueous liquor produced from Coronach lignite #3 at about 580°C is slightly acidic and this acidity presumably comes from partly oxygen-containing compounds such as lower molecular weight humic acids associated with lignites. It is also noteworthy that no acidic components appear to exist in the aqueous liquor obtained at about 650°C with Coronach lignite #3. Low pH values of aqueous liquors derived from acid washed Coronach lignite #3 are presumably due to some organic and/or inorganic acids.

Aqueous liquors derived from low rank coals were kept in plastic bottles at ambient temperature. During storage, the aqueous liquors, as a rule, spontaneously discoloured. Initially they were colourless and then prone to redden on exposure to air and/or light and finally turned brown. However, the pH values hardly changed regardless of their colour changes.

The aqueous liquors obtained from pilot plant pyrolyses were analyzed for organic compound contents using GC/MS. Conditions used for GC/MS analysis are the same as those given previously.

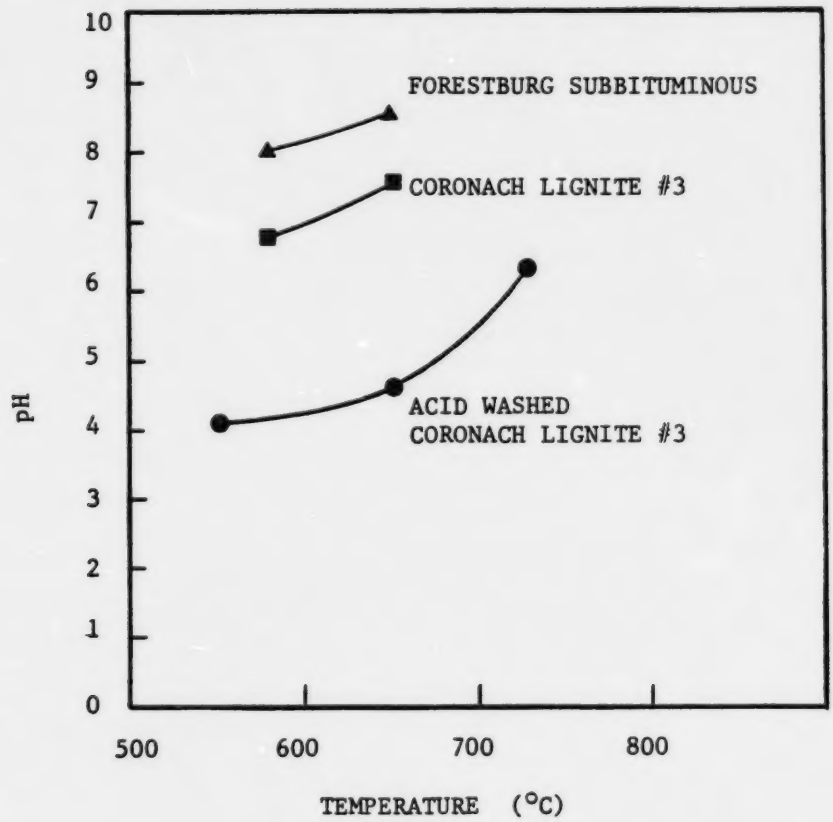


Fig. 6.21. PH of aqueous liquor, pilot plant pyrolysis, low rank coals.

Total ion chromatograms for organic compounds in the aqueous liquors derived from Forestburg subbituminous coal, and from the original and acid washed Coronach lignites are given in Figures 6.22, 6.23, and 6.24, respectively.

Three organic compounds, namely phenol, cresol and catechol, were separated and identified using the National Bureau of Standards data bank, containing approximately 25,000 spectra. As seen in Figures 6.22 to 6.24, phenol was found to be the most abundant component of the three. Cresol was the second largest peak except for acid washed Coronach lignite #3. In the aqueous liquor from Run P-84 which was conducted using the acid washed coal at 553°C, the peak of catechol (1,2-benzenediol) was observed to be as high as that of phenol. The darkening of these solutions when exposed to air and light is also typical of the presence of benzenediols.

Analytical results for the various aqueous liquors are summarized in Table 6.8. The number of ion counts corresponding to each peak was provided by the mass spectrometer analysis and this number is included in Table 6.8. Separate response factors for each component are required if the analysis is to be made quantitative.

It appears that the number of ion counts corresponding to each component does not necessarily correlate with the pH of the aqueous liquor. Therefore, it is likely that trace amounts of

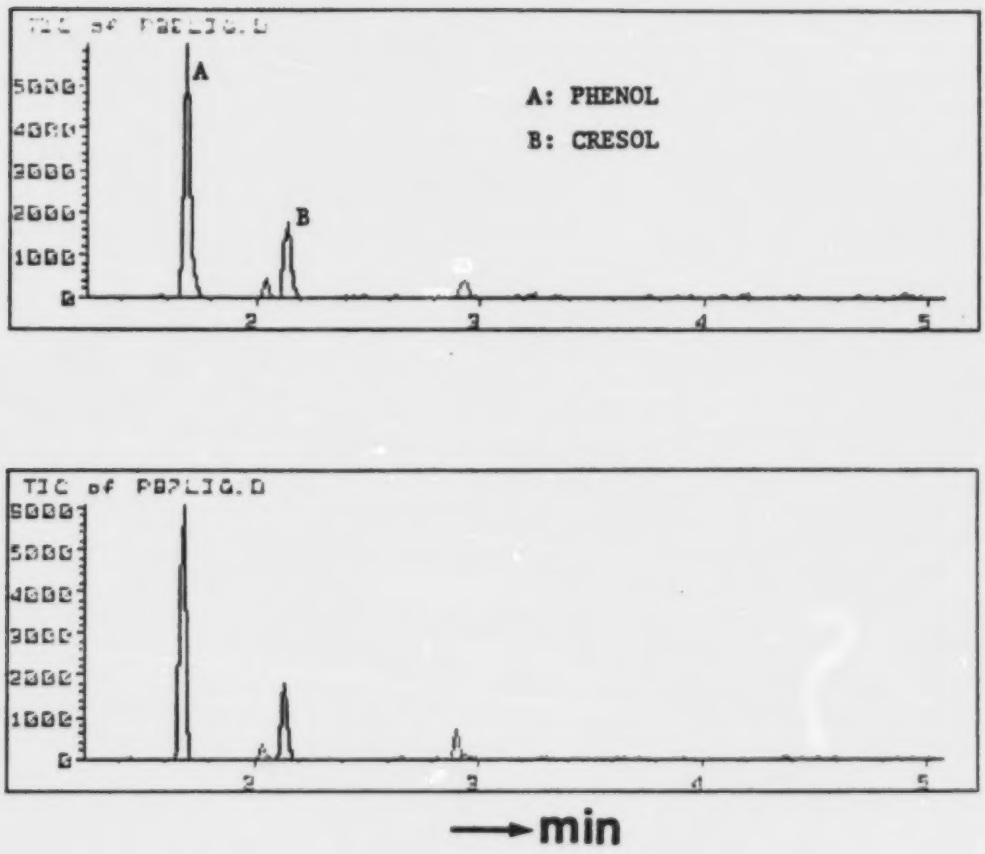


Fig. 6.22. GC/MS analysis of organic compounds in aqueous liquor, pilot plant pyrolysis, Forestburg subbituminous coal, Runs P-86 and P-87.

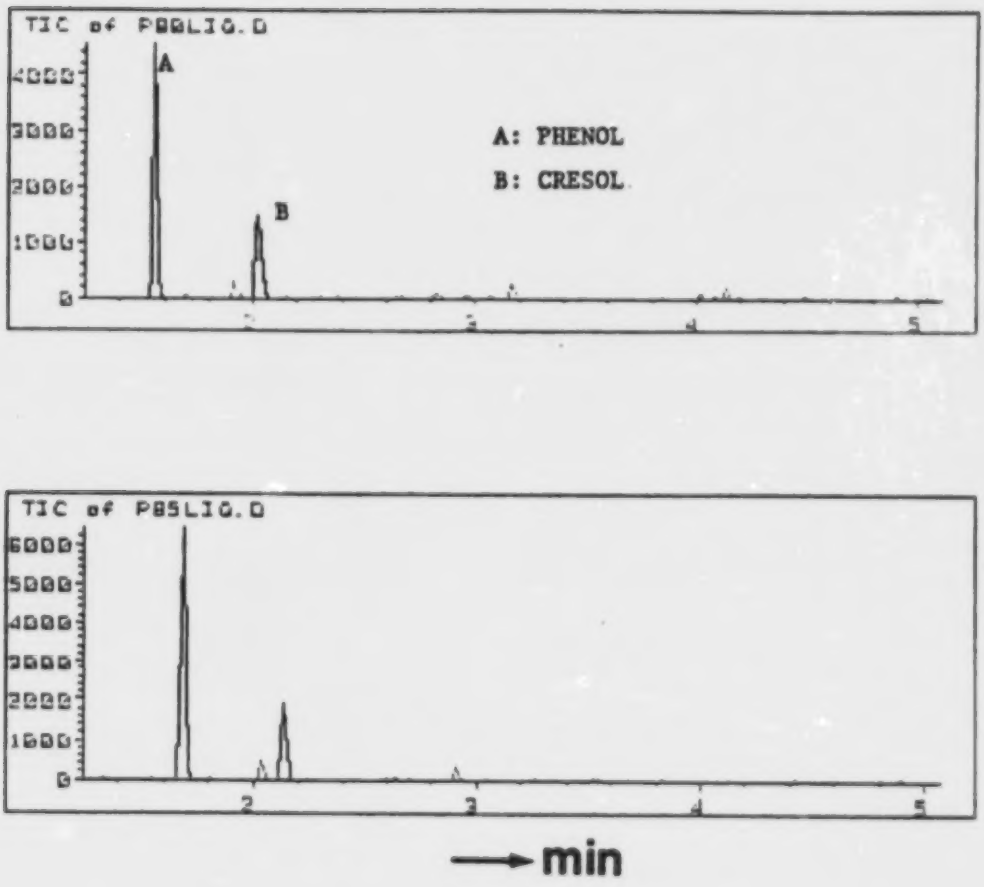


Fig.6.23. GC/MS analysis of organic compounds in aqueous liquor, pilot plant pyrolysis, Coronach lignite #3, Runs P-80 and P-85.

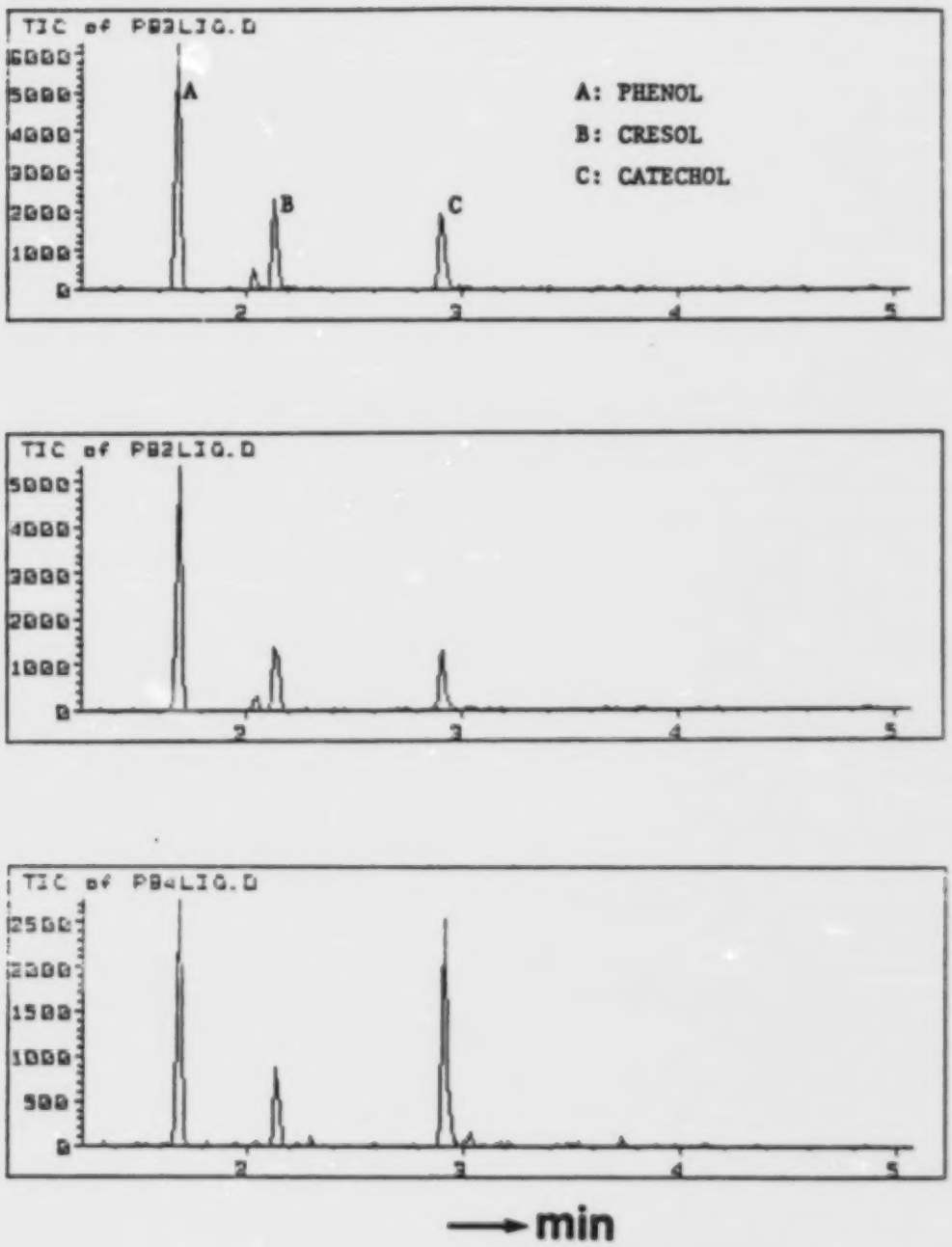


Fig.6.24. GC/MS analysis of organic compounds in aqueous liquor, pilot plant pyrolysis, acid washed Coronach lignite #3, Runs P-83, P-82, and P-84.

Table 6.8. Organic compounds in aqueous liquor, pilot plant pyrolysis, low rank coals.

	Forestburg sub-bituminous		Coronach lignite #3				
			acid washed			original	
	P-87	P-86	P-84	P-82	P-83	P-85	P-80
pH	7.97	8.48	4.11	4.63	6.39	6.75	7.49
H2O content (wt %)	99.37	97.39	96.12	96.82	99.11	98.40	96.75
	Number of ion counts for each component(x10,000)						
Phenol	9.05	9.92	3.39	8.09	7.99	8.47	6.45
m/p-Cresol	2.81	3.34	1.35	2.00	3.27	2.71	2.32
Catechol	tr	tr	4.08	2.16	3.65	tr	tr
Total	11.86	13.26	8.72	12.25	14.91	11.18	8.77

Notes: 1. pH measurement by Digital pH meter E632 (METROHM Ltd.,Switzerland).

2. H2O content determination by Karl-Fischer titration, Brickmann Model 633.

3. Compound identification by GC/MS (Hewlett-Packard5970 mass selective detector).

4. Number of ion counts based on a total ion chromatogram of 0.5 μl of aqueous liquor.

5. tr = trace amounts.

compounds, which were not detected by GC/MS, are the main factor controlling the pH of aqueous liquor.

6.5 DETERMINATION OF ELEMENTAL COMPOSITION

6.5.1 Elemental Mass Balance in Pyrolysis

Carbon, hydrogen and oxygen balances for pilot plant runs are respectively. The results are given as the percentage of a given element which was contained in the final products, such as gas, tar, char and water. All oxygen values reported in Table 6.11 are obtained by difference, and therefore contain all the overall mass balance errors, as well as the analytical errors. As seen in Table 6.11, the oxygen balance closures in Runs P-79, P-77, P-80, P-87 and P-86 gave extraordinarily large values presumably due to the underestimated values in carbon and hydrogen analyses. Table 6.11 also indicates that the percentage of oxygen for char is extremely variable compared to the other products. This diversity in the percentage of oxygen in char can also be partly attributed to the porous and hygroscopic characteristics associated with chars which make them capable of absorbing oxygen and water from the air (5).

Tables 6.9 and 6.10 show that the final balance closures for carbon and hydrogen are largely between 90% and 110%. It can also be observed that most of the carbon is found in the char and the carbon conversion to char increases with decreasing temperature

Table 6.9. Mass balance for carbon, pilot plant pyrolysis.

Run	Coal	Temp.	Res. time	Feed rate	100(mass of C in products) / mass of C fed			
		(°C)	(s)	(kg/h)	Gas	Tar	Char	Total
P-72	#2	555	0.49	1.601	6.27	6.34	81.40	94.02
P-71	#2	651	0.47	1.546	10.32	16.48	75.44	102.24
P-74	#2	712	0.47	1.326	12.95	15.10	71.66	99.70
P-76	#2	651	0.45	1.124	9.83	15.38	80.38	105.58
P-79	#2	653	0.44	1.467	10.50	14.42	66.13	91.05
P-77	#2	648	0.44	2.846	10.63	12.17	71.69	94.49
P-78	#2	656	0.35	1.840	9.06	14.39	72.88	96.33
P-75	#2	615	0.44	1.633	8.74	13.59	73.08	95.41
P-85	#3	581	0.46	1.635	7.72	13.51	79.46	100.69
P-80	#3	652	0.45	1.590	10.01	18.76	64.18	92.95
P-84	A	553	0.50	1.657	8.57	16.70	70.42	95.69
P-82	A	652	0.46	1.535	8.99	22.29	76.56	107.84
P-83	A	732	0.41	1.577	13.60	19.73	79.38	112.71
P-87	F	582	0.47	1.798	6.93	16.06	83.78	106.77
P-86	F	651	0.45	1.787	9.47	19.10	67.62	96.19

Notes: #2 = Coronach lignite #2
#3 = Coronach lignite #3
F = Forestburg subbituminous coal
A = Acid washed Coronach lignite #3

Table 6.10. Mass balance for hydrogen, pilot plant pyrolysis.

Run	Coal	T(°C)	100(mass of H in products) / mass of H fed				
			Gas	Tar	Char	Water	Total
P-72	#2	555	8.82	9.90	53.33	26.18	98.24
P-71	#2	651	14.37	24.95	39.22	28.25	106.80
P-74	#2	712	17.76	20.95	30.60	23.46	92.66
P-76	#2	651	12.21	22.75	38.14	21.50	94.59
P-79	#2	653	14.83	22.46	34.46	25.85	97.60
P-77	#2	648	14.11	19.42	38.84	23.15	95.52
P-78	#2	656	19.08	23.32	37.46	27.92	107.78
P-75	#2	615	9.74	20.27	38.82	19.66	88.49
P-85	#3	581	10.61	21.97	42.64	16.20	91.42
P-80	#3	652	15.08	26.51	31.53	21.58	94.70
P-84	A	553	15.94	25.57	40.28	25.22	107.01
P-82	A	652	12.96	34.68	34.85	20.14	102.63
P-83	A	732	20.12	28.24	29.21	33.27	110.84
P-87	F	582	14.36	26.55	44.18	26.73	111.82
P-86	F	651	20.83	29.51	30.38	30.03	110.75

Notes: #2 = Coronach lignite #2
#3 = Coronach lignite #3
A = Acid washed Coronach lignite #3
F = Forestburg subbituminous coal

Table 6.11. Mass balance for oxygen, pilot plant pyrolysis.

Run	Coal	T(°C)	100(mass of O in products) / mass of O fed				
			Gas	Tar	Char	Water	Total
P-72	#2	555	26.13	5.18	51.84	33.96	117.12
P-71	#2	651	35.57	9.95	30.54	36.72	113.83
P-74	#2	712	42.85	9.25	7.95	30.44	90.50
P-76	#2	651	35.57	6.21	30.42	27.81	100.00
P-79	#2	653	38.78	10.13	53.70	33.60	136.21
P-77	#2	648	41.18	7.63	45.53	30.08	124.42
P-78	#2	656	25.26	9.22	46.56	36.20	117.24
P-75	#2	615	35.48	9.44	46.34	25.24	116.50
P-85	#3	581	29.26	8.41	44.48	20.05	102.20
P-80	#3	652	34.48	12.05	50.68	26.75	123.96
P-84	A	553	24.66	10.90	51.02	26.23	112.81
P-82	A	652	26.46	13.05	20.78	21.00	81.29
P-83	A	732	36.87	11.27	10.97	34.64	93.75
P-87	F	582	24.73	9.24	48.63	36.22	118.82
P-86	F	651	28.91	10.26	40.62	40.79	120.58

Notes: #2 = Coronach lignite #2
#3 = Coronach lignite #3
A = Acid washed Coronach lignite #3
F = Forestburg subbituminous coal

except for the acid washed Coronach lignite #3. Table 6.10 indicates that from 20% to 35% of the hydrogen appears in the tar and that the hydrogen conversion to tar is almost the same as that to water. Table 6.11 shows that only 5% to 13% of the original oxygen content was retained in the tar and the rest was rejected as gas, char,and water. From 20% to 40% of the oxygen was converted to water at the expense of the hydrogen and the loss of hydrogen as water reached 16% to 33% of hydrogen present in the original coal, as shown in Table 6.10. A selective use of the hydrogen for tar has been and will continue to be a major focus of interest in the liquefaction of coal.

6.5.2 Elemental Composition of Pyrolysis Products

Table 6.12 gives the percentages of carbon and hydrogen contained in pyrolysis products from Coronach lignite #2, and Table 6.13 gives the percentages of carbon and hydrogen in products from original and acid washed Coronach lignite #3 and Forestburg subbituminous coal.

The results shown in Tables 6.12 and 6.13 indicate that carbon content of the products increases with temperature in all cases. The hydrogen content of the gases, except for the acid washed Coronach lignite #3, increases with temperature while the hydrogen content of the chars decreases steadily. The hydrogen content of the tars generally decreases with the temperature increase, except for the data obtained at about 550°C. The trends

Table 6.12. Carbon and hydrogen analyses of products, effect of temperature, pilot plant pyrolysis, Coronach lignite #2.

Residence time = 0.47-0.49s.
Feed rate = 1.326-1.601kg/h.

Run	T(°C)		C %	H %
P-72	555	Gas	36.50	3.30
		Tar	69.29	6.93
		Char	76.61	3.22
P-71	651	Gas	40.75	3.65
		Tar	73.86	7.17
		Char	82.94	2.77
P-74	712	Gas	41.72	3.67
		Tar	73.77	6.58
		Char	91.95	2.52

Table 6.13. Carbon and hydrogen analyses of products, effect of temperature, pilot plant pyrolysis, low rank coals.

Residence time = 0.41-0.50s.
Feed rate = 1.535-1.798kg/h.

Run	Coal	T(°C)		Gas	Tar	Char
P-84	A	553	C %	39.50	70.12	71.12
			H %	4.70	6.84	2.59
P-82	A	652	C %	39.37	71.28	85.23
			H %	3.61	6.69	2.48
P-83	A	732	C %	41.20	71.79	90.94
			H %	3.88	6.54	2.14
P-85	#3	581	C %	37.06	72.08	77.76
			H %	3.35	7.70	2.75
P-80	#3	652	C %	39.04	72.12	72.42
			H %	3.87	7.07	2.34
P-87	F	582	C %	39.75	74.10	78.14
			H %	5.40	8.03	2.70
P-86	F	651	C %	43.07	75.10	78.45
			H %	6.22	7.61	2.31

Notes: A = acid washed Coronach lignite #3.
#3 = Coronach lignite #3.
F = Forestburg subbituminous coal.

shown in Table 6.12 are in general agreement with the data obtained from the bench scale unit (8).

Table 6.13 indicates that the carbon content of the tars and gases is not significantly affected by coal type, by acid washing, and by pyrolysis temperature. In contrast, the hydrogen content of the tars and gases is fairly dependent on the coal type and acid washing pretreatment. The H/C atomic ratio of tars obtained from low rank coals is summarized in Figure 6.25.

From Figure 6.25, it is indicated that the H/C ratio decreases steadily with temperature increase in all cases. This is consistent with the previous data reported by Scott et al. (8). Figure 6.25 also indicates that the Forestburg tar has the highest H/C ratio while the acid washed Coronach #3 tar has the lowest H/C ratio. The Coronach #3 tar has a higher H/C ratio than Coronach #2 tar under equivalent pyrolysis conditions. This higher H/C ratio of Coronach #3 tar might be ascribed to a possibility of moisture being trapped in the pore structure and thus participating in the pyrolysis reactions as if it was a hydrogen donor. This behaviour of natural moisture in rapid pyrolysis was also pointed out by Suuberg et al. (12) with a North Dakota lignite. It has also been suggested that drying low rank coal results in a reduction in reactivity of the coal, so that the changes in behaviour of dried coals may be the result of reactions taking place during the coal drying process.

It is also shown in Figure 6.25 that the H/C ratio of tar produced from Coronach lignite #2 at a residence time of 0.35 seconds is the highest of all tars which were produced at about 650°C. It would also appear that the H/C ratio of tars increased with increasing the feed rate of coal at a pyrolysis temperature of 650°C.

Table 6.14 gives the contents of carbon and hydrogen in pyrolysis products obtained at different feed rates, and shows that the carbon content of tar and char increases markedly at a low feed rate of 1.124 kg/h and that the effect of feed rate on the hydrogen content of pyrolysis products is less significant than it is on their carbon content.

From these observations it is concluded that a hydrogen-rich tar in terms of the H/C ratio can be produced at specific operating conditions, such as lower temperature, shorter residence time and higher feed rate, and that the types of coal and also the acid washing treatment of coal have significant effects on the elemental composition of tars derived from pilot plant pyrolysis.

6.5.3 Elemental Mass Balance in Solvent Fractionation

Table 6.15 gives elemental mass balances in solvent fractionation. The results of the mass balances for carbon and hydrogen shown in Table 6.15 indicate that the carbon balance closures gave higher values than 100% while the hydrogen balance closures were largely less than 100%. The deficiencies in hydrogen balance

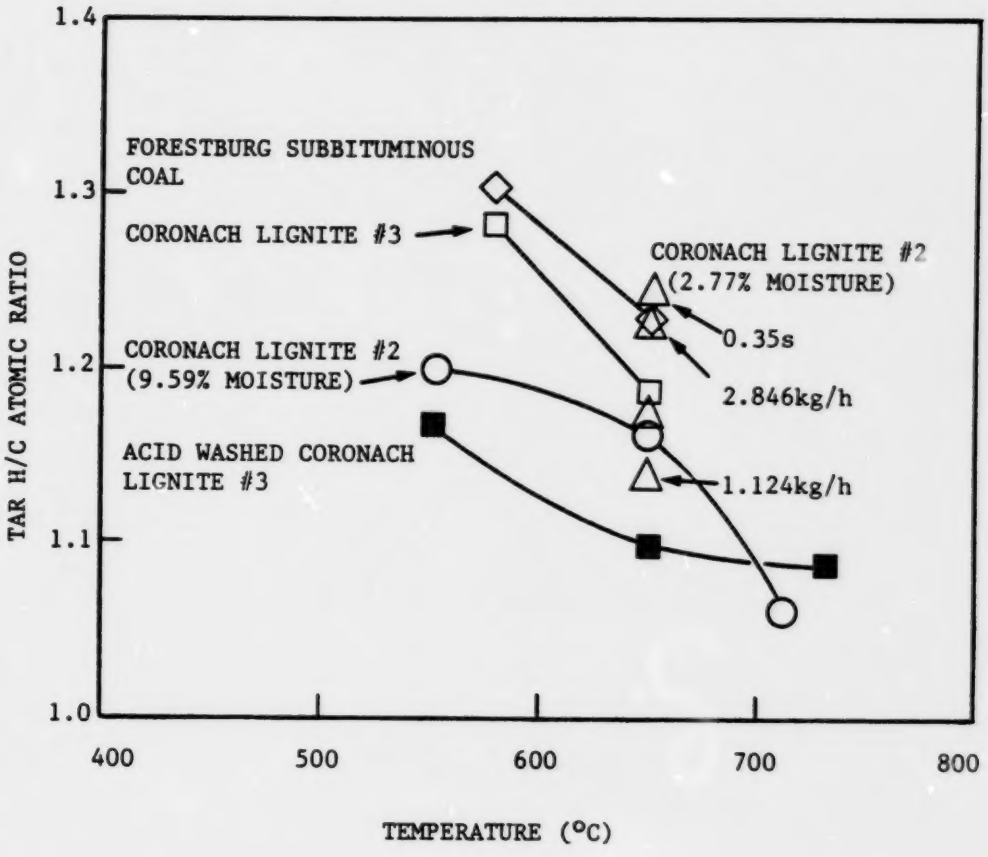


Fig. 6.25. Atomic H/C ratio of tars (summary) pilot plant pyrolysis, low rank coals.

Feed rate = 1.47-1.84kg/h unless otherwise specified.
Residence time = 0.41-0.50seconds unless otherwise specified.

Table 6.14. Carbon and hydrogen analyses of products, effect of feed rate, pilot plant pyrolysis, Coronach lignite #2.

Residence time = 0.44-0.45s.
Temperature = 648-656°C.

Run	Feed rate (kg/h)		C %	H %
P-76	1.124	Gas	39.82	3.17
		Tar	78.42	7.44
		Char	84.01	2.56
P-79	1.467	Gas	39.19	3.55
		Tar	71.81	7.16
		Char	73.20	2.45
P-77	2.846	Gas	38.20	3.25
		Tar	73.44	7.50
		Char	77.17	2.68

Table 6.15. Elemental mass balance, solvent fractionation, pilot plant pyrolysis, Coronach lignite #2.

Oil = pentane soluble
Asphaltene = pentane insoluble, toluene soluble
Preasphaltene = toluene insoluble

Run	T(°C)		Oil	Asph.	Preasph.	Total
P-72	555	C %	26.4	52.2	28.0	106.7
		H %	32.0	49.1	19.2	100.3
		N %	9.4	33.5	23.0	65.9
		O %	9.3	39.5	33.0	81.9
P-70 *	646	C %	32.2	41.4	30.4	104.0
		H %	33.9	32.2	18.9	84.7
		N %	11.8	47.2	41.0	100.0
		O %	12.6	41.3	36.6	90.4
P-71	651	C %	36.8	48.9	18.7	104.4
		H %	43.2	41.8	12.6	97.6
		N %	7.4	37.0	22.2	66.7
		O %	15.9	47.7	21.6	85.1
P-74	712	C %	27.5	57.3	20.6	105.5
		H %	30.4	51.7	15.0	97.1
		N %	3.3	47.4	24.5	75.0
		O %	8.8	48.5	24.0	81.1

Note: * THF injected in top of reactor.

closures could be attributed to understated hydrogen content in oil fractions because oil fractions consist of substantial amounts of volatile components and these volatiles generally contain more hydrogen than do the high-boiling-point compounds.

The micro analytical techniques currently in use for elemental analysis in the present analytical work (Perkin-Elmer 240C Analyzer) were reported to be less ideal for heterogeneous materials like char and coal (5). These techniques also seem to be unsuitable for C/H/N/S determinations of volatile matters like light hydrocarbons. The use of only a few milligrams of sample makes it extremely difficult to avoid spontaneous evaporation loss of low-boiling-point components in oil fraction samples during sampling operations.

The results of the mass balances for nitrogen and oxygen are also shown in Table 6.15. The nitrogen balance closures give extraordinarily low values. These results suggest that the analytical method such as that done using Perkin-Elmer 240C Analyzer is far from ideal for determination of nitrogen, or else that volatile compounds containing nitrogen are not accounted for in the determination of nitrogen content.

Table 6.15 also indicates that the oxygen balance closures give lower values than 100%. It should be again remembered that all oxygen values reported are obtained by difference and therefore contain all the overall mass balance errors, as well as the

errors due to analytical errors. In contrast to the oxygen balance closures in pyrolysis products, which gave extraordinarily large values, as large as 120% to 130%, the oxygen balance closures in solvent fractionation vary between 81% and 91%. Two possibilities may explain the deficiencies in the oxygen balances. One possibility is overestimated carbon contents as mentioned above. The other possibility is a loss of oxygenated compounds contained in oil fractions. It is likely that both of these are involved at the same time in the errors in oxygen balances.

6.5.4 Elemental Composition of Solvent Fractions

Table 6.16 gives the contents of carbon and hydrogen in solvent fractions of Coronach lignite #2 tars, together with their H/C atomic ratio. Oil, asphaltene and preasphaltene fractions were obtained by the solvent fractionation method described previously. The oil fraction is the pentane-soluble fraction and the asphaltene fraction is the pentane-insoluble toluene-soluble fraction.

The results of the carbon analyses of solvent fractions shown in Table 6.16 indicate that the carbon content of each fraction increases with increasing temperature. The oil fraction was found to have the highest carbon content of the three solvent fractions at all temperatures tested. The effect of THF injection on the carbon content of solvent fractions appears to be of minor significance.

Table 6.16. Carbon and hydrogen analysis of solvent fractions, pilot plant pyrolysis, Coronach lignite #2.

Oil = pentane soluble
Asphaltene = pentane insoluble, toluene soluble
Preasphaltene = toluene insoluble

Run	T(°C)		Oil	Asph.	Preasph.
P-72	555	C %	80.48	74.00	68.16
		H %	9.80	6.96	4.68
		atomic H/C	1.46	1.13	0.82
P-70*	646	C %	81.93	74.10	72.22
		H %	9.78	6.53	5.09
		atomic H/C	1.43	1.06	0.85
P-71	651	C %	81.84	75.24	73.37
		H %	9.29	6.25	4.87
		atomic H/C	1.36	0.98	0.80
P-74	712	C %	84.85	76.61	72.69
		H %	8.35	6.16	4.72
		atomic H/C	1.18	0.96	0.78

Note: * THF injected in top of reactor.
THF: C_4H_8O ; C 66.63% ; H 11.18% ; O 22.19%.

The results of the hydrogen analyses of solvent fractions shown in Table 6.16 indicate that the hydrogen contents ofthe oil and asphaltene fractions decreases with temperature while that of the preasphaltene fraction appears to be temperature independent. The hydrogen content of each fraction appears to be increased slightly by injection of THF into the reactor. This fact suggests a possibility of THF participating in the pyrolysis process as if it is a hydrogen donor.

The data for the atomic H/C ratios shown in Table 6.16 indicates that the H/C ratio of oil and asphaltene fractions decreases steadily with temperature while that of preasphaltene fractions decreases only slightly with temperature. The H/C atomic ratio increases almost equally in all fractions when adding THF into the reactor. This fact may suggest that THF becomes highly reactive under the pyrolysis conditions and thus generates hydrogen-rich reaction products. This higher H/C ratio of the reaction products, such as oil, asphaltene and preasphaltene fractions, seems to be reasonable considering the fact that THF itself has a high H/C ratio of 2. From a viewpoint of producing better quality liquids, the addition of hydrogen-rich reactive compounds, such as THF might be an attractive possibility for future investigation.

6.5.5 Elemental Mass Balance for Methanol Fractionation of Preasphaltene

Table 6.17 gives the elemental mass balances for methanol extraction of preasphaltene fractions from pilot plant runs P-70, P-71, P-72 and P-74. The methanol-soluble fraction could contain polar oxygenated compounds formed from the humic acid portions of the lignite. Both methanol-soluble and methanol-insoluble fractions were recovered in a solid form after removing methanol.

As the results in Table 6.17 show, the carbon and hydrogen balance closures for the products of methanol fractionation gave values between 94% and 98%. Almost identical balance closures of C and H reflect fairly accurate carbon/hydrogen analyses for the methanol soluble and insoluble fractions.

In contrast to chars, for which analytical problems have been reported, the methanol soluble and insoluble fractions appear to be comparatively suitable for the micro analytical techniques currently employed for elemental analysis. The above-mentioned results may imply that these fractions obtained from methanol fractionation possess basically homogeneous structure in their solid forms. On the other hand, the oxygen balance closures varied between 111% and 122%. These data suggest that the methanol soluble and insoluble fractions were presumably oxidized by the air during the methanol fractionation operations.

Table 6.17. Elemental mass balance, methanol fractionation of preasphaltene, pilot plant pyrolysis, Coronach lignite #2.

Run	T(°C)		Methanol soluble	Methanol insoluble	Total
P-72	555	C %	61.69	33.82	95.51
		H %	66.88	28.85	95.73
		N %	45.69	45.69	91.38
		O %	64.19	48.73	112.92
P-70*	646	C %	43.04	51.92	94.96
		H %	49.31	48.33	97.64
		N %	34.42	53.02	87.44
		O %	55.60	64.02	119.62
P-71	651	C %	47.58	49.26	96.84
		H %	52.98	44.97	97.95
		N %	49.30	66.20	115.50
		O %	49.26	61.60	110.86
P-74	712	C %	49.86	44.90	94.76
		H %	56.57	37.08	93.65
		N %	49.51	31.55	81.06
		O %	58.30	63.61	121.91

Note: * THF injected in top of reactor.

From the results reported in earlier sections, only the preasphaltene yield markedly increased when THF was injected into the reactor, leaving the oil and asphaltene yields unchanged. From this evidence, it is suggested that THF participates in pyrolysis reactions to generate the preasphaltene fraction, and thus prevents secondary charification reactions between reactive radical fragments. Consequently, the char yield in Run P-70 decreased by approximately 10% on a basis of maf coal. The results shown in Table 6.17 appear to reflect the secondary reaction between THF and volatile fragments, which is slightly favorable to the formation of the methanol-insoluble fraction.

6.5.6 Elemental Composition of Methanol Soluble and Insoluble Fractions

Table 6.18 gives the results of the determination of carbon and hydrogen in methanol fractionation products derived from preasphaltene fractions. The results indicate that the contents of carbon and hydrogen of both methanol soluble and insoluble fractions are somewhat temperature independent. This trend is consistent with that of preasphaltene fractions, which did not present any tendency with temperature.

Table 6.18 also indicates that the carbon content decreases when adding THF into the reactor. This result may be due to a low carbon content of THF, which has a carbon content of 66.63%. In contrast to the carbon content, the hydrogen content of each fraction increases when injecting THF into the reactor. This

Table 6.18. Carbon and hydrogen analyses, methanol fractionation of preasphaltene, pilot plant pyrolysis, Coronach lignite #2.

Run	T(°C)		Methanol soluble	Methanol insoluble
P-72	555	C %	67.38	61.29
		H %	5.02	3.59
		atomic H/C	0.89	0.70
P-70*	646	C %	67.94	69.12
		H %	5.48	4.53
		atomic H/C	0.97	0.79
P-71	651	C %	72.42	69.77
		H %	5.35	4.22
		atomic H/C	0.89	0.73
P-74	712	C %	69.83	67.86
		H %	5.14	3.63
		atomic H/C	0.88	0.64

Note: * THF injected in top of reactor.
THF: C_4H_8O ; C 66.63% ; H 11.18% ; O 22.19%.

increase in the hydrogen content could be ascribed to a high hydrogen content of THF, which has a hydrogen content of 11.18%.

The H/C atomic ratio of each fraction is included in Table 6.18. The data show that every methanol-soluble fraction has a higher H/C ratio compared with the methanol-insoluble fraction at evert temperature tested. Apparently, hydrogen-rich components in the preasphaltene fraction were selectively extracted by methanol and consequently less hydrogen-rich components were left in the methanol-insoluble fraction.

Temperature effects on the H/C ratio of the methanol fractions appear to be less important compared to those of the other solvent fractions, such as oil and asphaltene fractions, the H/C ratio of which presented a relatively strong dependency on temperature.

An H/C ratio less than 1.0 generally corresponds to polycyclic aromatic compounds, which may infer that the preasphaltene fraction consists mainly of polycyclic aromatic compounds and their oxygenated derivatives.

Table 6.18 also shows that the methanol-insoluble fractions, except for Run P-70 with THF injection into the reactor, have a hydrogen-deficient composition compared to the original coal, the H/C ratio of which is 0.77.

Although the chemical composition of the methanol soluble part of preasphaltene has not been elucidated precisely, it is expected that this fraction consists primarily of polar compounds having oxygenated functional groups, such as hydroxy ketones, acids, hydroxy acids, and so on. As regards their molecular size, they are possibly high molecular weight, but may also be of low molecular weight, a postulate suggested by the fact that this part of the preasphaltene is highly soluble in methanol regardless of its polymer-like appearance.

7. CATALYTIC HYDROPYROLYSIS

7.1 Introduction

Devolatilization of coal under conditions which yield very fast particle heating rates (>10^3 °C/s) maximizes the release and evaporation of organic species from the coal structure. These volatiles are reactive and require rapid quenching to minimize secondary retrogressive reactions and maximize yields of condensible liquids. Coal hydropyrolysis is defined as pyrolysis under hydrogen pressure and involves the thermal decomposition of coal macerals followed by evolution and cracking of volatiles in hydrogen.

Previous researchers have established that when pyrolysis is conducted under H_2 pressure, the H_2 reacts with and stabilizes the volatilized species to give a higher degree of devolatilization in low rank coals than pyrolysis in an inert atmosphere.

The catalytic hydropyrolysis of coal at one atmosphere of hydrogen pressure under fast heating conditions was investigated in previous work using a bench scale fluidized bed reactor containing catalyst as a fluid-bed medium (5). The initial results with a Co/Mo catalyst showed that this process modification was a potentially promising approach. Some further tests were carried out in the present study to indicate which specific catalysts, if any, deserve further detailed study.

7.2 RESULTS AND DISCUSSION - NON-CATALYTIC HYDROPYROLYSIS

7.2.1 Hydropyrolysis of Coronach Lignite #2

Hydropyrolysis of Coronach lignite #2 was carried out at about 650°C. Table 7.1 shows the effect of changing the atmosphere on product yields of pyrolysis. Run 216 under H_2 produced more gas (20.09% vs. 18.12%), less tar (10.65% vs. 13.59%), and less char (51.85% vs. 61.11%) when compared to the pilot plant pyrolysis P-79 performed under N_2. The water yield of Run 216 appears to be understated and this is reflected strongly in the deficiency of total yield. The decrease in tar and char yields under H_2 is consistent with previous data on Saskatchewan lignite (Scott, Piskorz, and Fouda (8).

It was found that a substantial amount of char remained in the fluid bed during the H_2 runs, namely 43% of char in Run 215 and 29% in Run 216. This may be partly attributed to the longer residence time of the H_2 runs, but it is also reported by Scott et al. (8) that chars largely remained in the fluid bed during H_2 runs at 0.45s residence time.

Since H_2 produced under a nitrogen atmosphere accounted for less than 0.5% of the yield, the H_2 produced during the H_2 runs is presumably insignificant in the material balance closure.

Table 7.1. Hydropyrolysis of Coronach lignite #2, bench scale reactor, Ottawa sand.

Run	200	215	216	P-79
Temperature(°C)	690	663	658	653
Sand particle size(μm)	-590 +300	-590 +300	-300 +250	-840 +590
Wt. of sand(g)	60	60	60	2100
Atmosphere	N_2	H_2	H_2	N_2 & Product Gas
Vapour residence time(s)	0.56	0.80	0.64	0.44
Coal particle size(μm)	-250 +74	-250 +74	-250 +74	-590 +62
Wt. of coal fed(g)	32.58	29.02	32.26	1893.0
Product yields, wt % maf coal				
Gas	25.06	18.28	20.09	18.12
Tar	15.86	10.64	10.65	13.59
Char	50.76	51.24	51.85	61.11
Water	8.75	13.84	11.08	10.11
Total	100.43	94.00	93.67	102.93
Gas yields, wt % maf coal				
H2	0.50	ND	ND	0.12
CO	9.13	8.60	10.00	6.64
CO2	11.40	5.80	5.43	9.05
CH4	2.36	2.44	2.91	1.75
C2H4	0.50	0.36	0.36	0.34
C2H6	0.21	0.28	0.25	0.10
C3	0.39	0.36	0.40	0.07
C4	0.57	0.44	0.29	0.06
BTX	ND	ND	0.44	ND
Total	25.06	18.28	20.09	18.12

Note: ND = not determined.

The results shown in Table 7.1 also indicate that a H_2 atmosphere promotes CO production and decreases CO_2 production. Although Run 200 performed under N_2 at 690°C is included in Table 7.1 for information only, it can be seen that C_1 to C_4 hydrocarbons for Run 200 are essentially the same compared to those for Run 215 and Run 216 under H_2. On the other hand, C_1 to C_4 hydrocarbons for Run 216 appear to be obtained in higher yields than the pilot plant run P-79.

A small particle size of sand, -300+250 mesh, was employed in Run 216 in an attempt to improve the fluidization of the sand bed. The results for the smaller sand size appear to be similar to those of Run 215 with the standard sand size. Therefore it is concluded that the effect of sand size on product yields is less significant than the other process variables.

7.2.2 Composition of Hydropyrolysis Tar

Since the amount of tar obtained from the bench scale unit was very small, products remaining in condensers were recovered by washing with THF. Tars from hydropyrolysis were subjected to GC analysis in solution form. The amount of THF in the solution was obtained from a calibration curve given in Figure 7.1. This amount was used to calculate the actual amount of tar injected into the GC analyzer.

Eight compounds were selected and compared with the results from the pilot plant pyrolysis performed under a N_2 atmosphere.

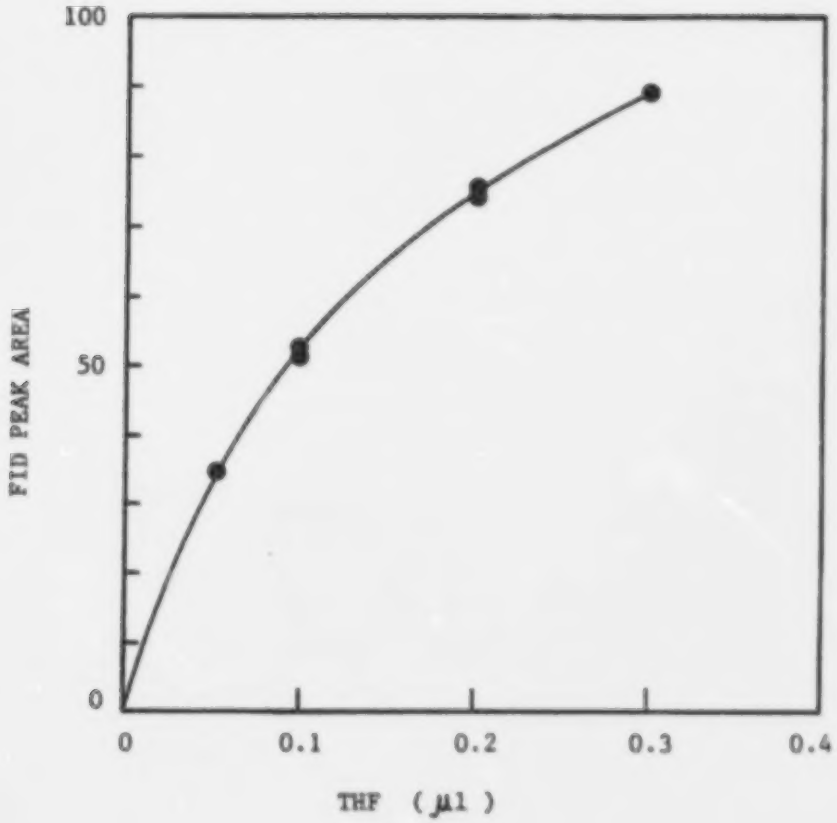


Fig.7.1. Calibration curve for THF.

Instrument: Perkin-Elmer Sigma 3B
Column: DB-5,30m x 0.5mm o.d.
Detector: FID at 290°C

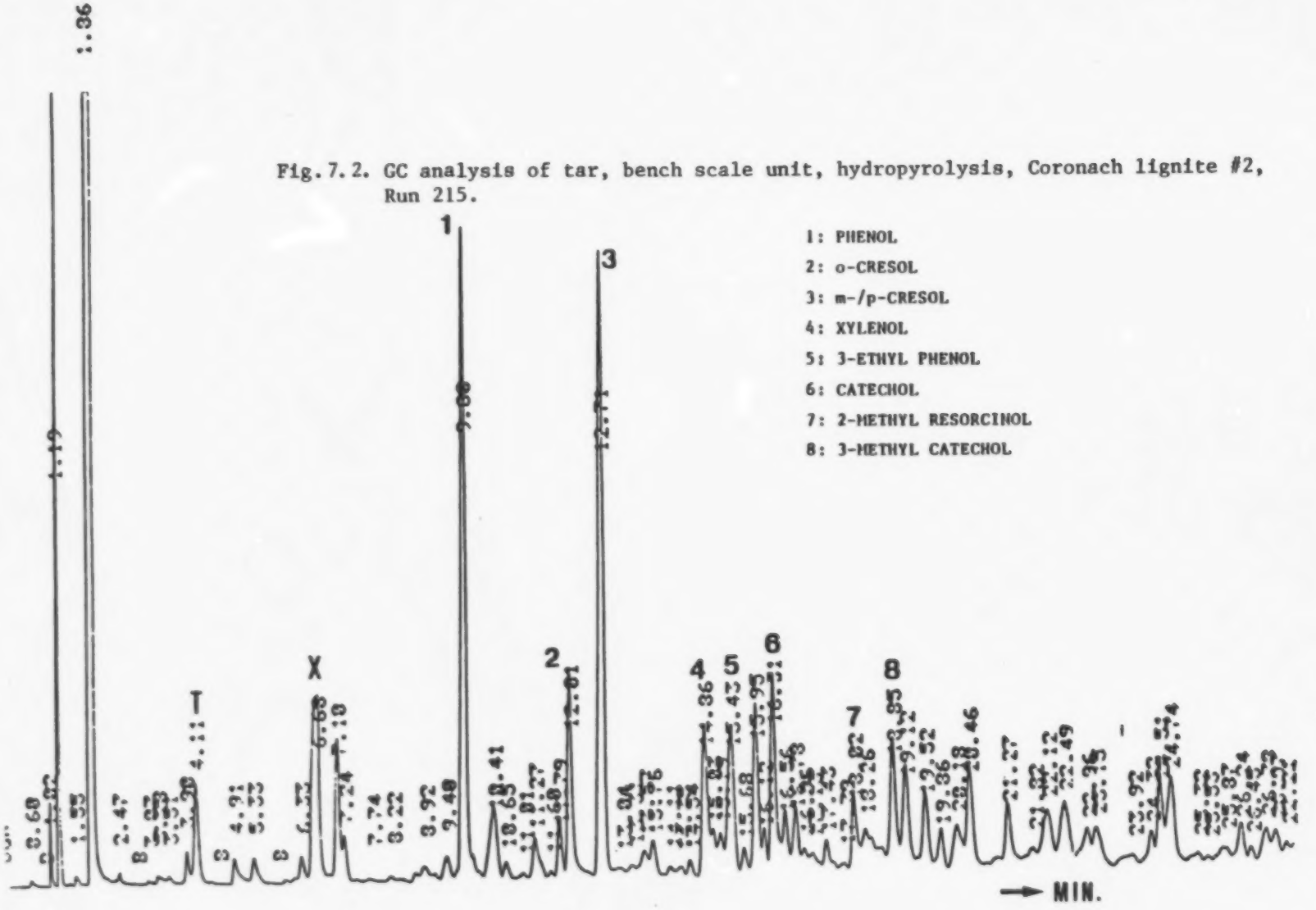
The results of GC analyses of tars from Runs 215, 216 and P-79 are shown in Figures 7.2, 7.3 and 7.4, respectively. These Figures clearly demonstrate that there exists a significant difference in tar composition between the two atmospheres, nitrogen and hydrogen.

The major compounds were semi-quantitatively determined in terms of corrected peak area for each compound. The corrected peak areas of the eight prominent components are given in Table 7.2. These results indicate that phenol and m/p-cresol are present in significantly greater quantities in the hydropyrolysis tars. In contrast, catechol (1,2-benzenediol) and methyl catechol decreased markedly in hydropyrolysis from 1.58 to 0.64-0.93, and from 1.05 to 0.48-0.73, respectively.

While o-cresol increased in hydropyrolysis from 0.25 to 0.60-0.62, methyl resorcinol decreased from 0.60 to 0.27-0.31. This fact suggests that methyl resorcinol reacted with hydrogen to produce o-cresol and water almost exclusively. In a similar way, it is likely that catechol and methyl catechol were hydrogenated to yield phenol and m/p-cresol, respectively.

The higher yield of phenols from lignite is consistent with that found by Wu and Harrison (22) who studied pyrolysis and hydropyrolysis of Louisiana lignites under atmospheric pressure. Their products also contained substantial amounts of benzenes and aliphatic hydrocarbons in terms of normalized ion percentages

Fig. 7.2. GC analysis of tar, bench scale unit, hydropyrolysis, Coronach lignite #2, Run 215.



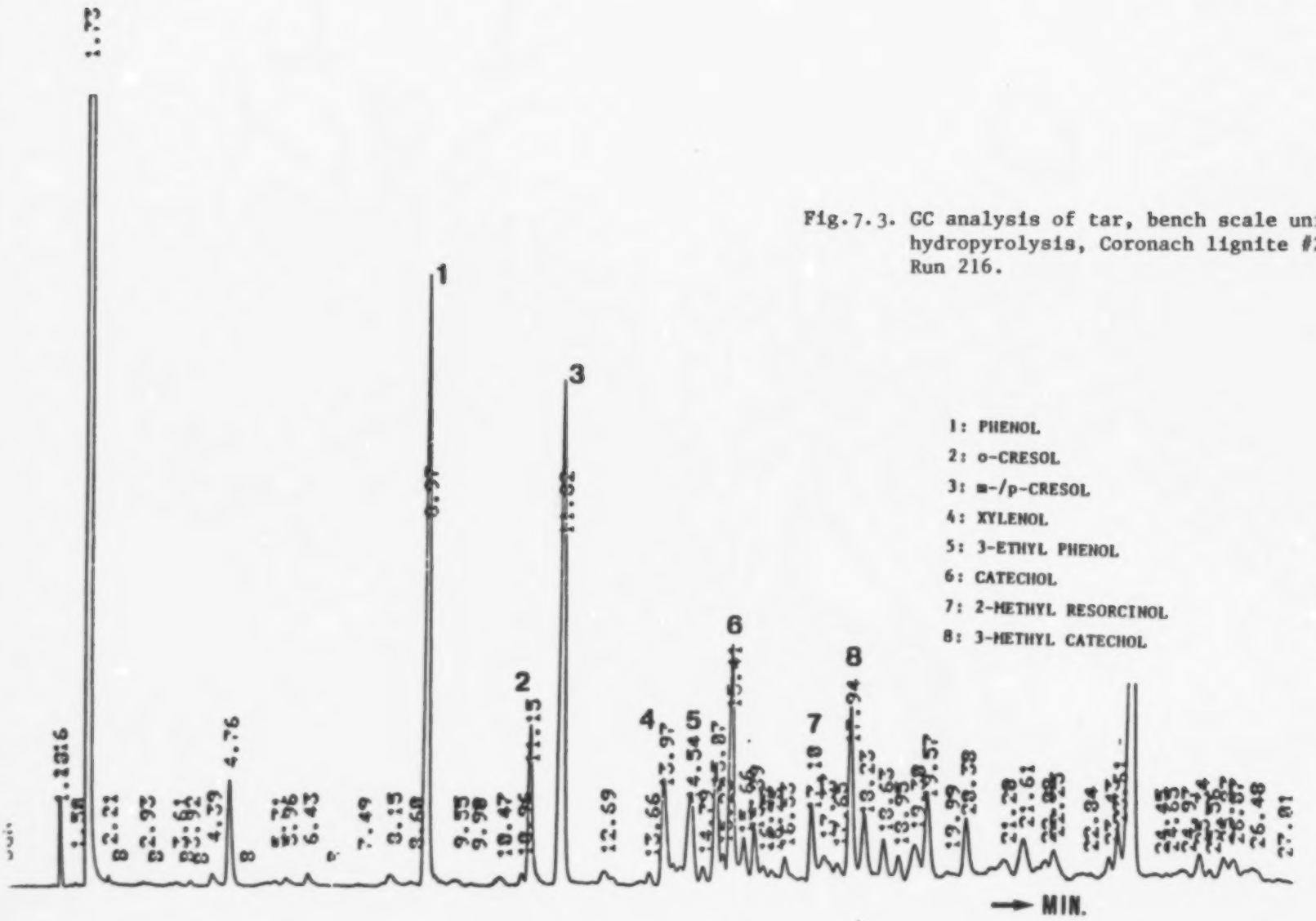


Fig.7.3. GC analysis of tar, bench scale unit, hydropyrolysis, Coronach lignite #2, Run 216.

Fig.7.4. GC analysis of tar, pilot plant pyrolysis in N2, Coronach lignite #2, Run P-79.

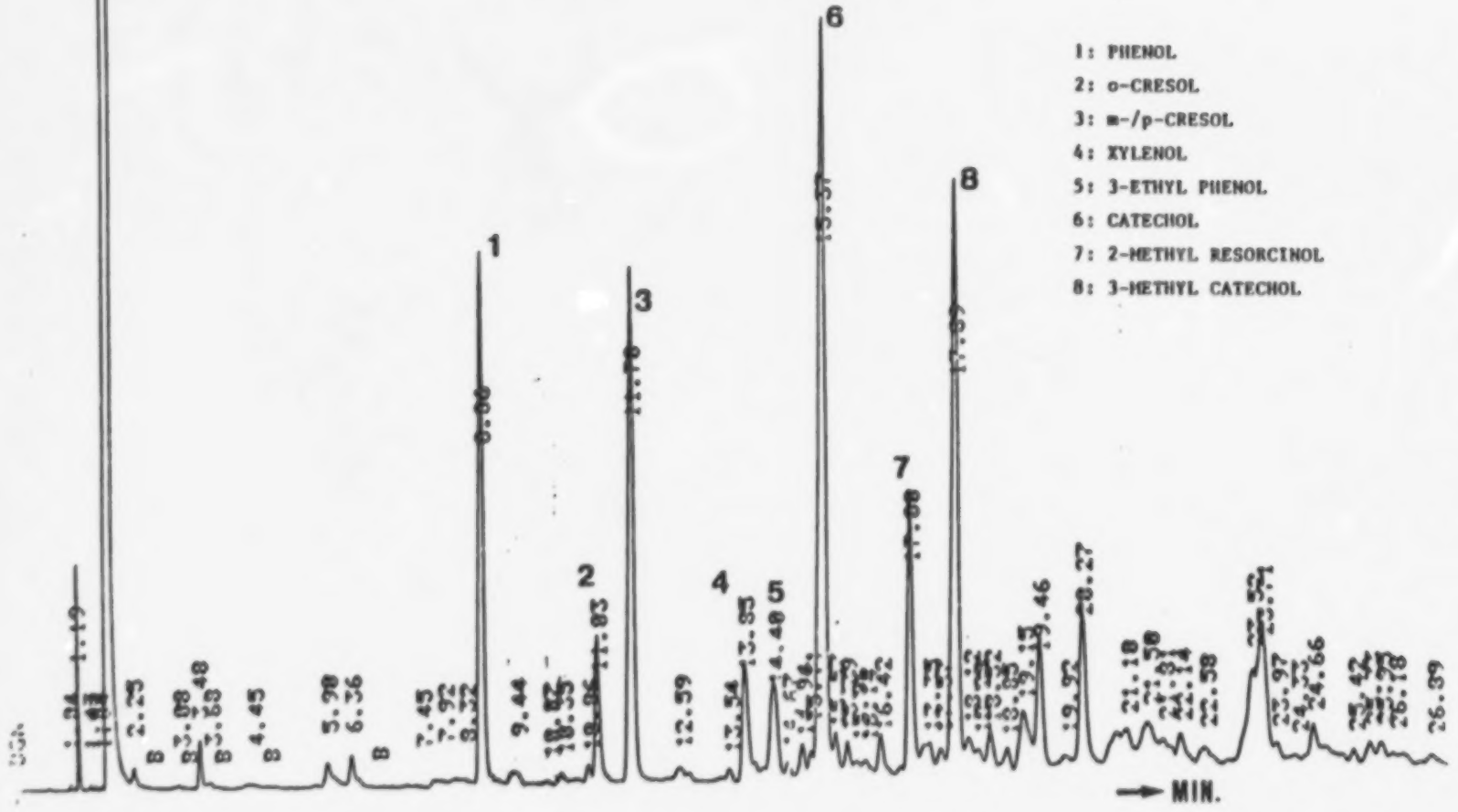


Table 7.2. Corrected peak area of prominent compounds in tar, bench scale unit, hydropyrolysis, Coronach lignite #2.

Run	215	216	P-79
Temperature(°C)	663	658	653
Atmosphere	H2	H2	N2
Compound, corrected peak area *1			
Phenol	1.91	2.21	0.77
o-Cresol	0.60	0.62	0.25
m/p-Cresol	2.01	2.10	0.88
Xylenol *2	0.53	0.59	0.26
Ethyl phenol	0.60	0.60	0.26
Catechol *3	0.64	0.93	1.58
Methyl resorcinol *4	0.27	0.31	0.60
Methyl catechol	0.48	0.73	1.05
Total	7.04	8.09	5.65

Notes:

*1 Corrected peak area $= \frac{\text{peak area by FID}}{0.3\mu l - \text{THF}(\mu l)} \times 0.2\mu l$

*2 Xylenol = dimethyl phenol
*3 Catechol = 1,2-benzenediol
*4 Resorcinol = 1,3-benzenediol

(NIP) provided by a mass spectrometer analysis. These product differences might be ascribed primarily to the differences in the original composition of lignites and secondarily to the differences in the analytical method and the pyrolysis condition. The altered tar composition in hydropyrolysis reconfirms the possibility suggested by Wu and Harrison that basic differences in reaction mechanisms exist in the two atmospheres.

7.2.3 Aqueous Liquor from Hydropyrolysis

Aqueous liquors from hydropyrolysis Run 215 and Run 216 were analyzed for their organic constituents by high resolution gas chromatography, with results as shown in Figures 7.5 and 7.6, respectively. Conditions for GC analysis are the same as those for tar.

The identification of each compound was performed on a basis of retention time. The overall composition of organic compounds present in the aqueous liquor was similar, in general, to that already found for hydropyrolysis tar. Figures 7.5 and 7.6 indicate that the major components are phenol and cresols. This result is the same as that observed previously with aqueous liquors from pilot plant pyrolyses under N_2.

Therefore, it can be concluded that the organic composition of aqueous liquor is essentially the same in both nitrogen and hydrogen atmospheres.

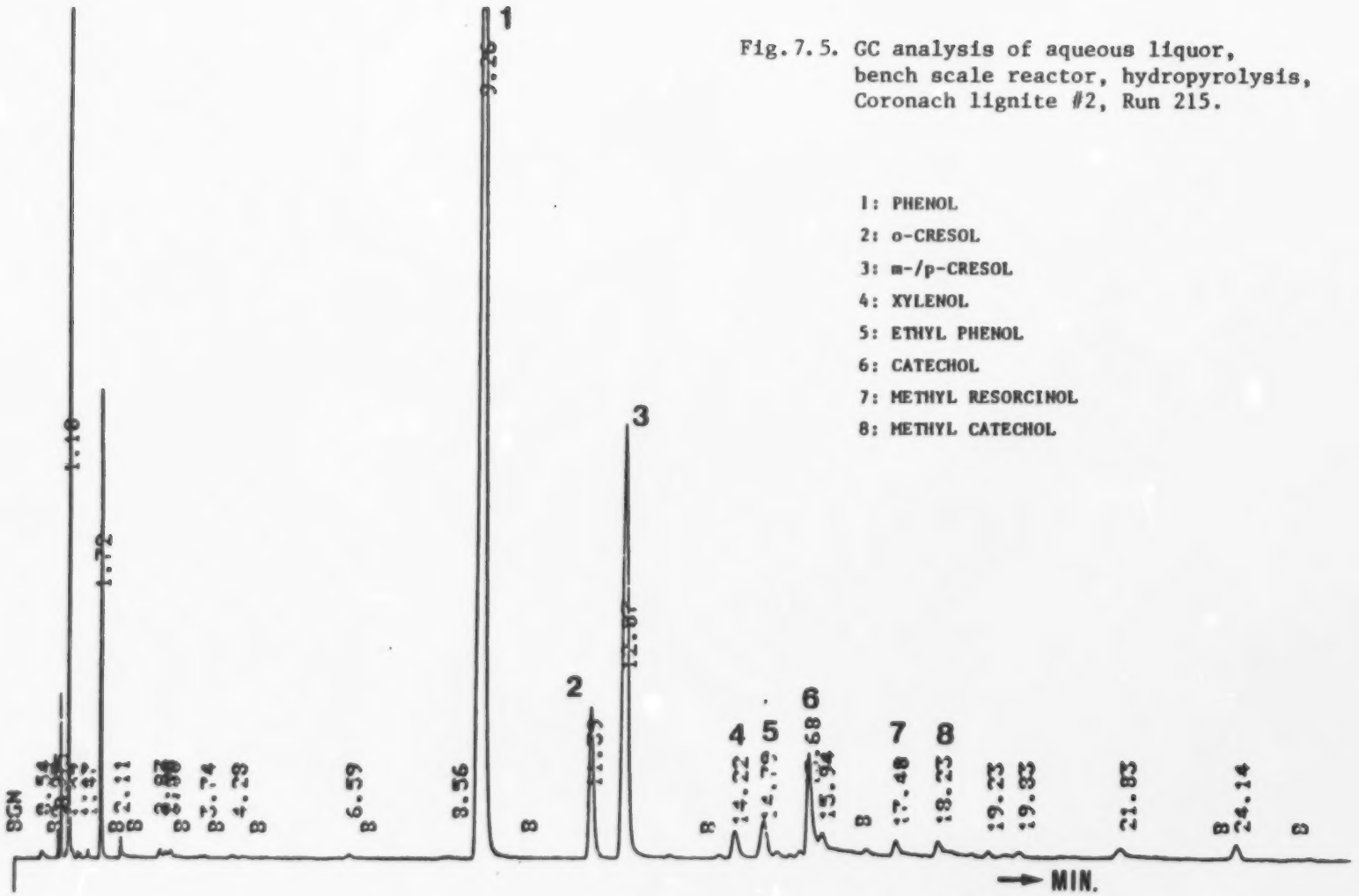
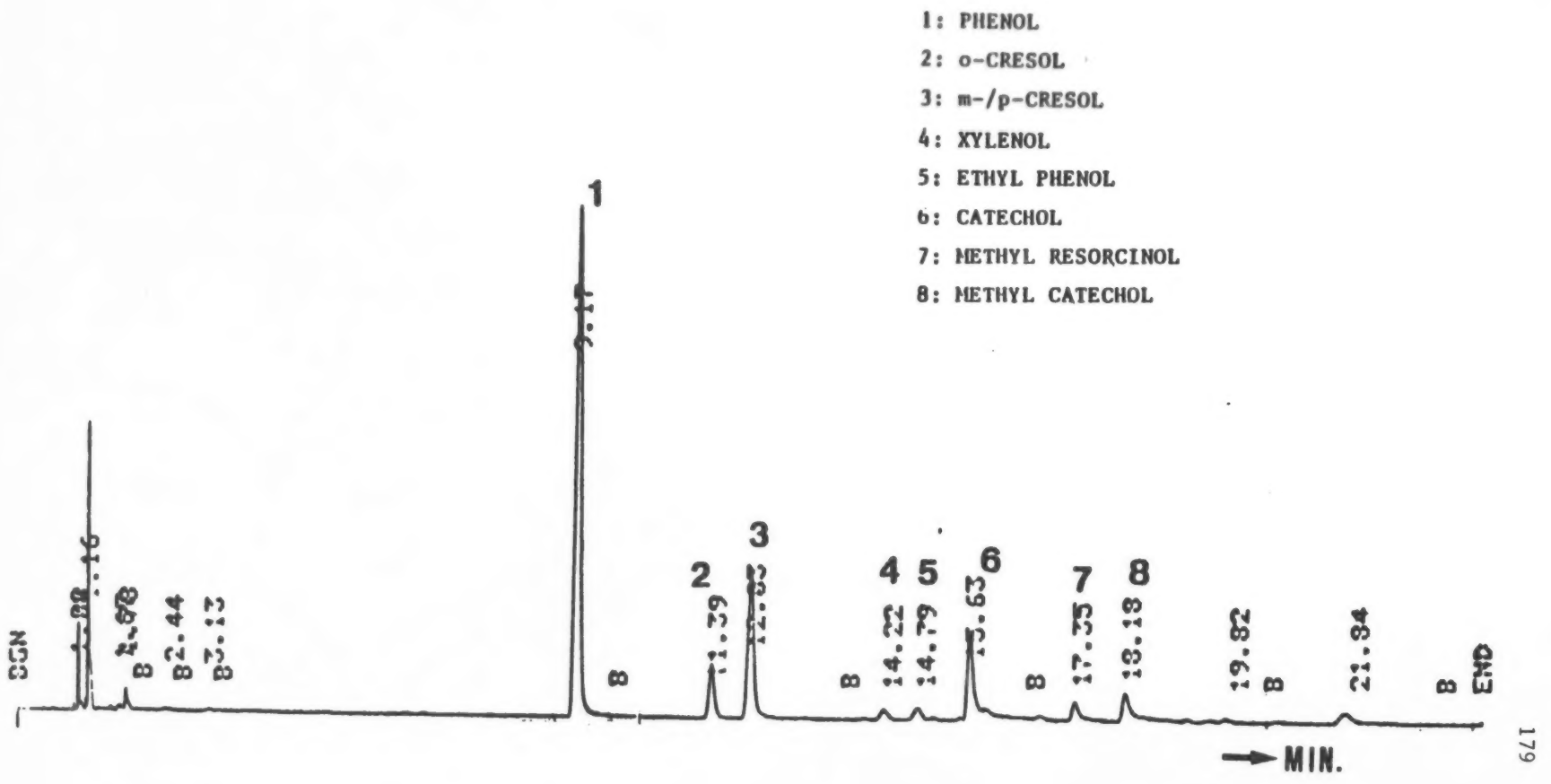


Fig. 7.5. GC analysis of aqueous liquor, bench scale reactor, hydropyrolysis, Coronach lignite #2, Run 215.

Fig. 7.6. GC analysis of aqueous liquor, bench scale unit, hydropyrolysis, Coronach lignite #2, Run 216.



7.3 RESULTS AND DISCUSSION - CATALYTIC HYDROPYROLYSIS

7.3.1 Catalyst Properties

Catalysts employed were nickel powder supplied by Sherritt Gordon Mines Ltd., Alberta and Ni on γ-Al_2O_3 methanation catalyst G-33RS supplied by United Catalysts Inc., U.S.A.

The composition and properties of the catalysts are given in Tables 7.3 and 7.4. The nickel powder sized to -300+149 μm contains trace amounts of impurities, such as cobalt, copper, iron, sulphur and carbon. This nickel powder was used without pretreatment since the effect of these impurities on the results of pyrolysis seemed to be insignificant in the present study. The G-33RS catalyst contained about 4% carbon. This carbon was found to cause a major difficulty in closing the carbon balance of the experiments (Scott (9). Therefore G-33RS catalyst was regenerated by passing air over the catalyst at a temperature of 650°C for 1 hour to burn out the carbon binder. The catalyst was then subjected to a reduction procedure.

The nickel catalyst was activated by the reduction of the nickel oxides present. Hydrogen was passed over the catalyst at a temperature of 650°C for 1 hour. The weight of the catalyst bed decreased from 55.15g to 38.87g through the regeneration and reduction operations. This reduced weight was used for calculating the material balance of the experiment. The weight reduction of the catalyst bed corresponds to the loss of moisture, oxygen

Table 7.3. Nickel powder.

Particle size : -50+100 mesh
-300+149 μm

Chemical analysis	wt %
Ni	99.7
Co	0.21
Cu	0.030
Fe	0.002
S	0.011
C	0.095
Apparent density	5.03 g/cc
True density (Ni)	8.90 g/cc

Note: Analysis by Sherritt Gordon Mines Ltd.,Alberta.

Table 7.4. Nickel catalyst, G33RS.

Chemical composition	wt %
Ni	36
S	< 0.05
C	3 - 5
Reduction(minimum)	40

Physical properties	
Bulk density(1/4x1/4in.)	1.04 g/cc
Surface area	45-75 m2/g
Pore volume (>29.2 Å)	0.25-0.35 cc/g
Crush strength,minimum average	9.07 kg
Particle density(1/8x1/8in.)*	2.27 g/cc

Notes: Analyses by United Catalysts Inc.,U.S.A.

* Measurement at U of W, as received.

and carbon present in the catalyst.

7.3.2 Catalytic Hydropyrolysis

The catalytic hydropyrolysis of lignite was investigated using a bench scale fluidized bed reactor containing catalyst as the fluidized bed medium.

Table 7.5 gives results of flash hydropyrolysis of Coronach lignite #2 conducted in the fluidized bed of each catalyst at atmospheric pressure. Table 7.5 includes, for comparison, data for hydropyrolysis in a sand bed.

The Ni catalyst resulted in only a minor change in char yield compared to the result of hydropyrolysis with sand in the bed. However, in the presence of catalyst as the fluidized bed medium, tar yields decreased from 10.65% maf coal to 8.28% with the nickel powder and to 4.15% with the Ni catalyst. The reduced tar yields can be attributed to secondary catalytic reactions of the evolving tar vapours. Table 7.5 also shows that gas yields increased from 20.22 % maf coal to 23.26% with the nickel powder and 25.98 % with the Ni catalyst. The yield of CO_2 in Run 226 with the nickel catalyst was somewhat lower than that in Run 216 with sand. The composition of the product gas in Run 226C appears surprisingly similar to that reported by Scott et al. (8) with a Co-Mo catalyst using two subbituminous coals, namely Forestburg and Hat Creek coals.

Table 7.5. Catalytic hydropyrolysis, bench scale reactor, Coronach lignite #2, H_2 at atmospheric pressure.

Run	216	220	226
Temperature(°C)	658	661	662
Bed material	sand	nickel	Ni/γ-Al_2O_3
Particle size,bed(μm)	-300+250	-300+149	-840+425
Wt. of bed material(g)	60.00	108.10	55.15
Vapour residence time(s)	0.64	0.60	0.51
Particle size,coal(μm)	-250+74	-250+74	-250+74
Wt. of coal fed(g)	32.26	39.68	14.83
Product yields (wt % maf coal)			
Gas	20.22	23.26	25.98
Tar	10.65	8.28	4.15
Char	51.85	52.37	49.02
Water	11.08	12.46	19.81
Total	93.80	96.37	98.96
Gaseous products (wt % maf coal)			
H2	0.13	2.97	5.78
CO	10.00	10.04	10.40
CO2	5.43	4.75	4.40
CH4	2.91	3.23	3.32
C2H4	0.36	0.54	0.58
C2H6	0.25	0.39	0.15
C3	0.40	0.39	0.40
C4	0.29	0.39	0.42
BTX	0.44	0.54	0.56
Total	20.22	23.26	25.98

Notes: (1) Run 216 = Ottawa sand.
(2) Run 220C = nickel powder supplied by Sherritt Gordon Mines Ltd.,Alberta.
(3) Run 226C = G33RS nickel catalyst supplied by United Catalyst Inc.,U.S.A.

Experimental data reported by CSIRO researchers, who conducted hydropyrolysis experiments using Ni-Mo and Co-Mo catalysts, also showed that there was little difference in the product gas composition between these two catalysts [Tyler and Nelson (23)].

It is apparent that the Ni catalyst was promoting the hydrogenation reaction to reduce the CO_2 content and increase the CO content but that the effect of the nickel powder on this reaction was less significant compared with the G-33RS nickel catalyst.

Table 7.5 also indicates that the use of the Ni catalyst as a fluidizing solid slightly increased methane yield and BTX yield. Also, in Run 226, it was observed that soot-like material was formed during the run.

In the present study it was very difficult to determine the composition of these condensation reaction products and identify with certainty the individual components, because of the complexity of the products coupled with the low concentration and also with small amounts of tar recovered from the bench scale unit.

7.3.3 Liquid Products from Catalytic Hydropyrolysis

Results of GC analyses for the tar products from catalytic hydropyrolysis Runs 220 and 226 are given in Figures 7.7 and 7.8, respectively. Eight major compounds were selected and semi-quantitatively determined by a flame ionization detector.

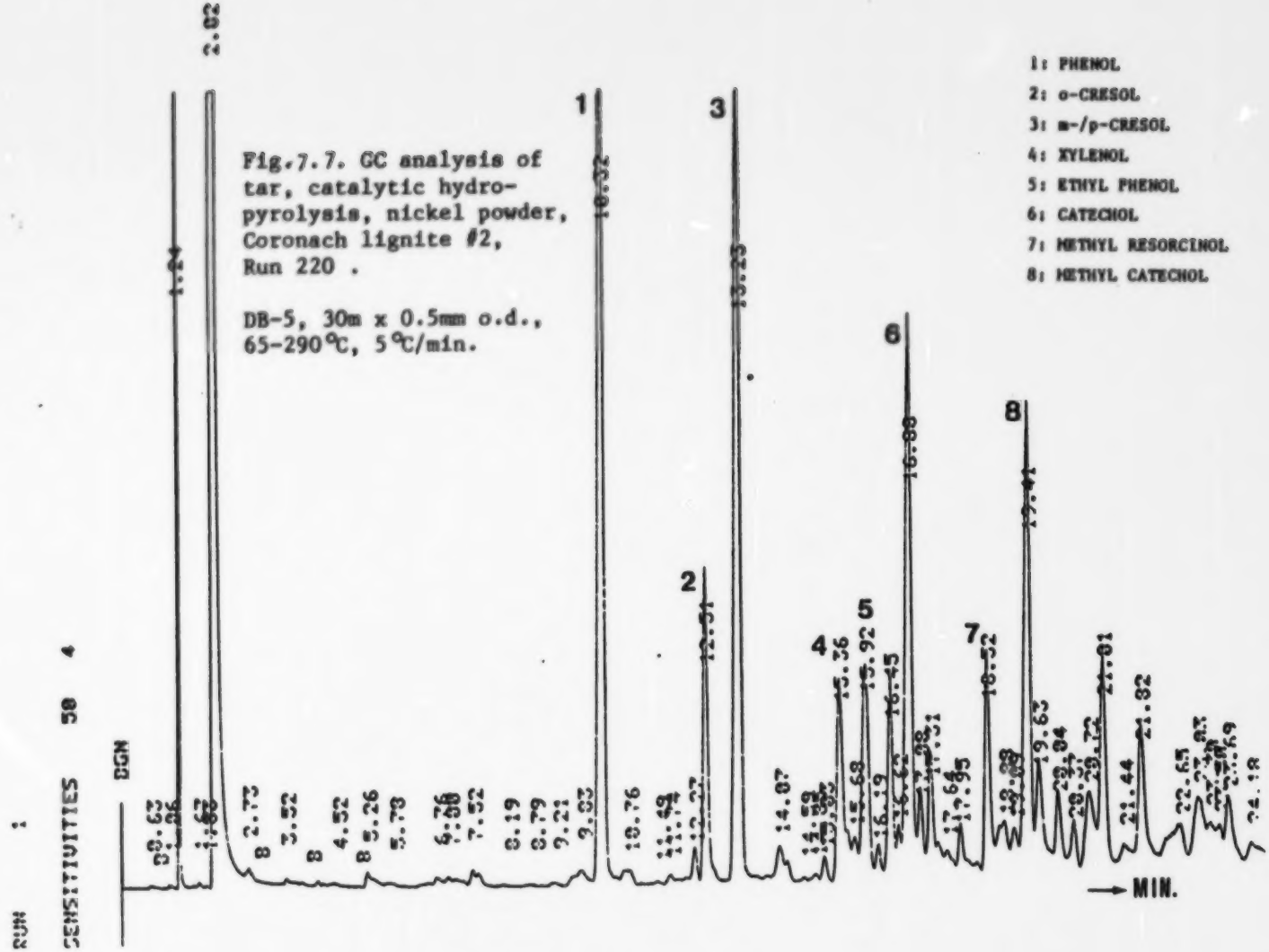


Fig.7.7. GC analysis of tar, catalytic hydropyrolysis, nickel powder, Coronach lignite #2, Run 220 .

DB-5, 30m x 0.5mm o.d., 65-290°C, 5°C/min.

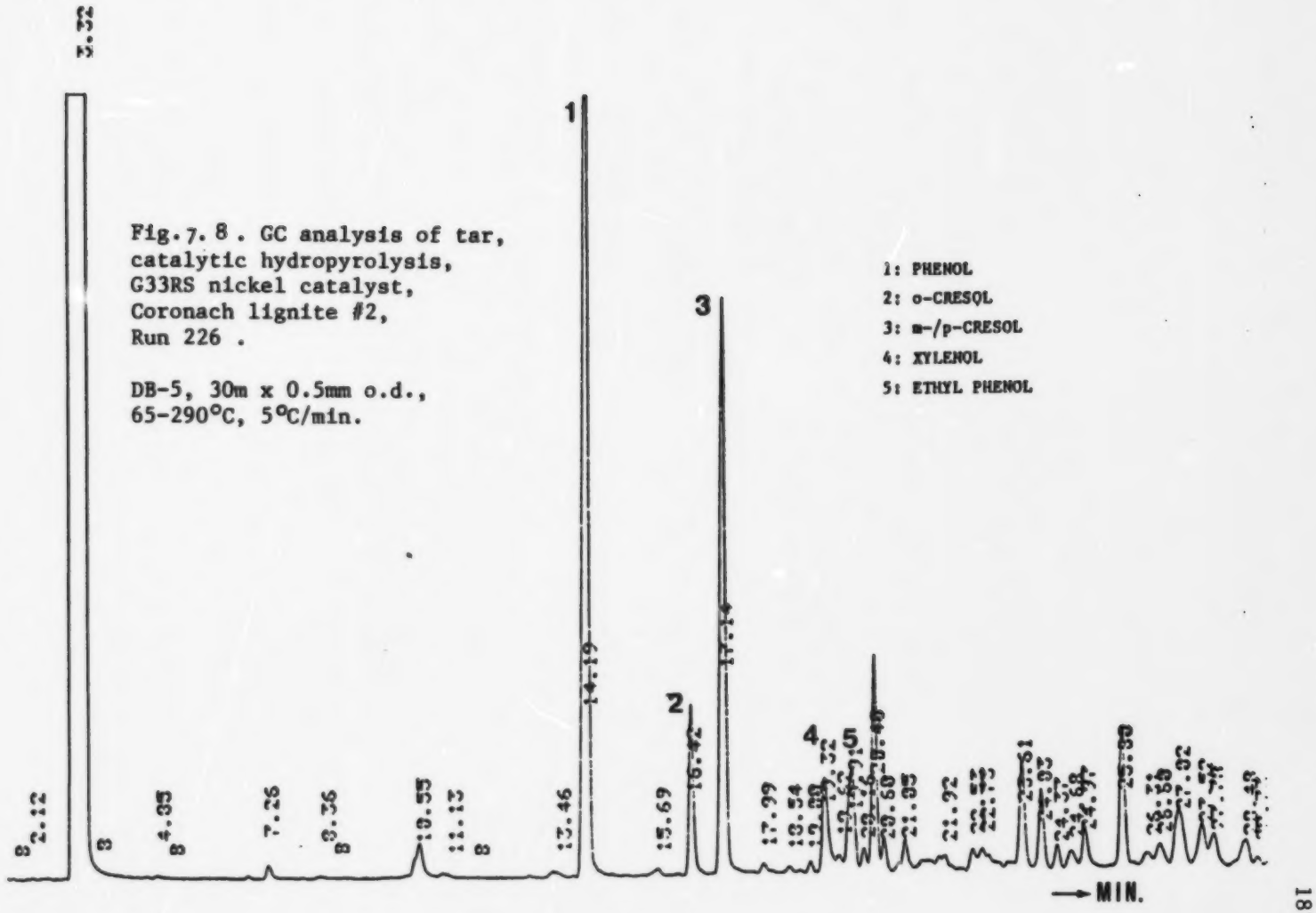


Fig. 7. 8 . GC analysis of tar, catalytic hydropyrolysis, G33RS nickel catalyst, Coronach lignite #2, Run 226 .

DB-5, 30m x 0.5mm o.d., 65-290°C, 5°C/min.

Separate response factors for each component are required if the analysis is to be made quantitative.

A comparison of results of the semi-quantitative analysis for each component is given in Table 7.6. These results suggest that the Ni catalyst caused the hydrocracking of dihydroxybenzenes, such as catechol and resorcinol, but the effect of this catalyst on the concentrations of phenols, although considerable, is less significant than its effect on the dihydroxybenzenes.

As mentioned in the previous section, yields of tar markedly decreased when pyrolyzing Coronach lignite #2 in the presence of catalyst as the fluidized bed medium. The results of the compositional analysis of tars shown in Table 7.6 indicate that the decrease in tar yields can be ascribed in part to the secondary reactions of the tar components. The greater part of the decrease in tar yields appears to be compensated for by the increase of water and gas yields (see Table 7.5).

Results of GC analyses for aqueous liquors from Runs 220 and 226 are given in Figures 7.11 and 7.12, respectively. The eight major compounds listed in Table 7.6 were all found in the liquor from Run 220 but dihydroxybenzenes were not found in the liquor from Run 226. These data appear to confirm the results of analyses of the tar products shown in Figures 7.9 and 7.10, as well as the conclusions reached from the data of Table 7.6.

Table 7.6. Concentrations of prominent components in tar, catalytic hydropyrolysis, H2 ,1 atm, Coronach lignite #2, -250+74 μm.

Run	216	220	226
Temperature(°C)	658	661	662
Bed material	Ottawa sand	Nickel powder	G33RS nickel catalyst
Compound	(tar yield,wt % maf coal)xCPA/100		
Phenol	0.235	0.175	0.172
o-Cresol	0.066	0.047	0.025
m/p-Cresol	0.224	0.159	0.099
Xylenol	0.063	0.045	0.020
Ethyl phenol	0.064	0.047	0.024
Catechol	0.099	0.110	tr
Methyl resorcinol	0.033	0.036	tr
Methyl catechol	0.078	0.092	tr
Total	0.862	0.711	0.340

Notes: CPA = corrected peak area

$$= \frac{\text{peak area detected by FID}}{\mu\text{l injected} - \mu\text{l of THF}} \times 0.2\,\mu\text{l}.$$

tr = trace amounts.

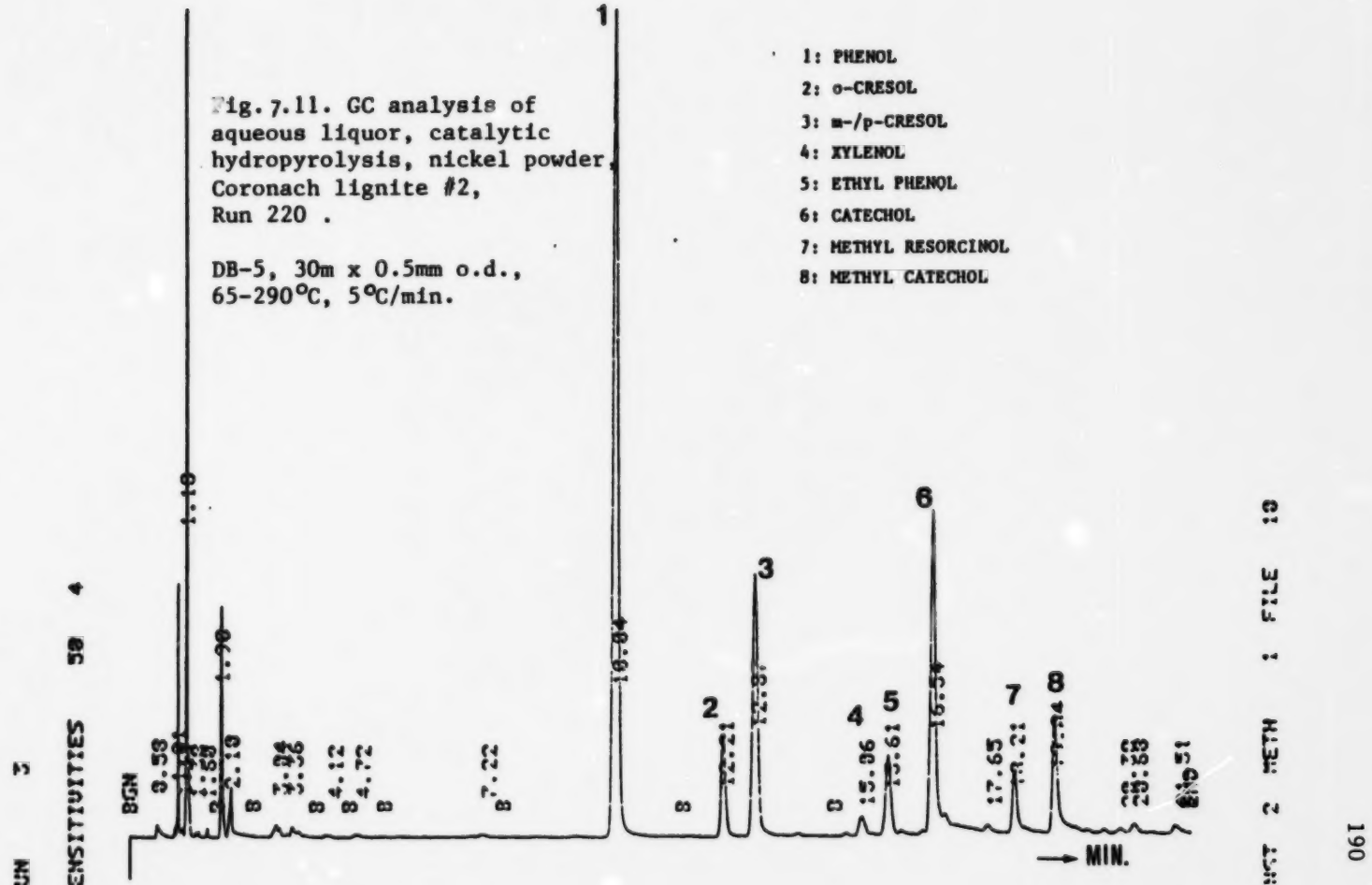
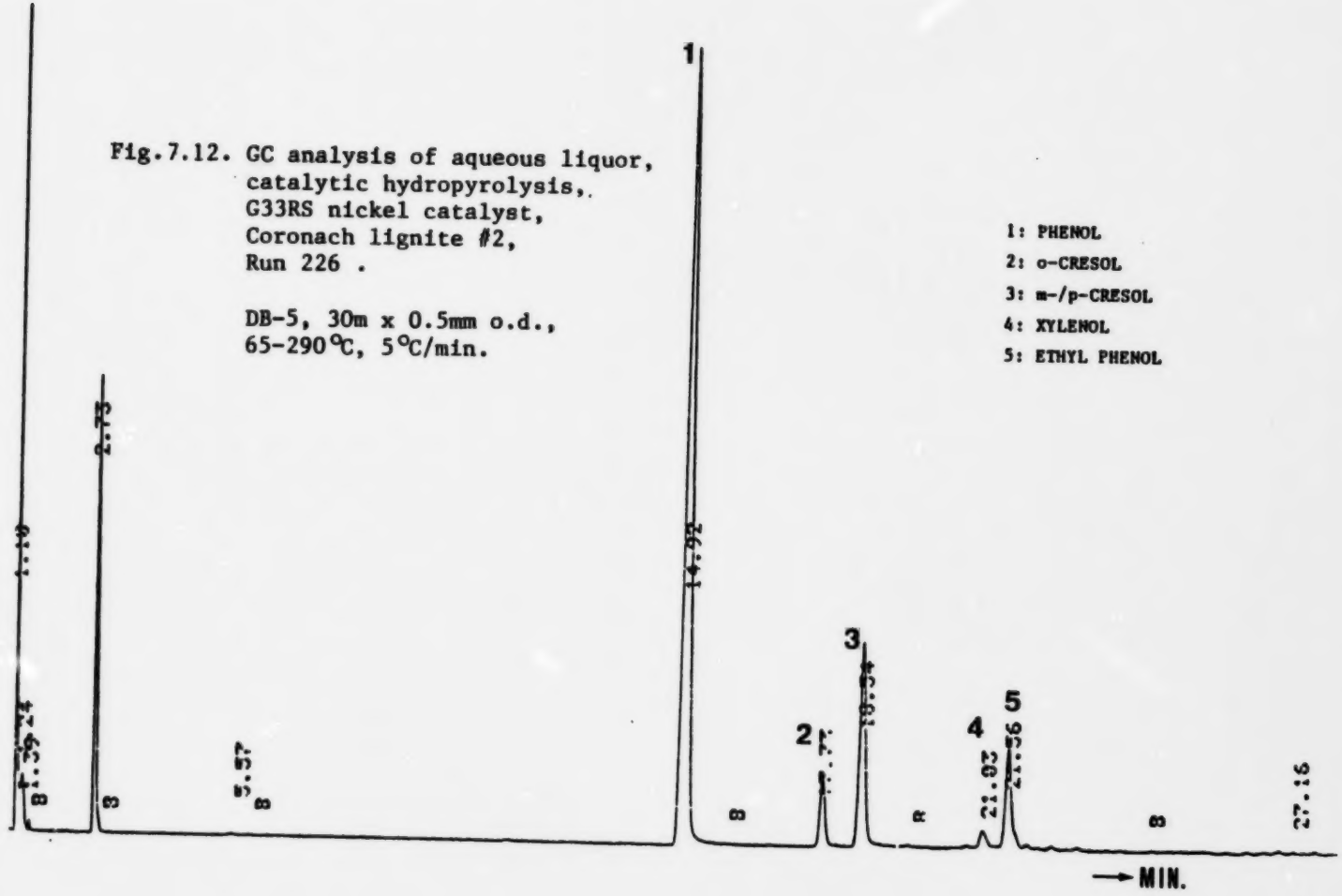


Fig. 7.11. GC analysis of aqueous liquor, catalytic hydropyrolysis, nickel powder, Coronach lignite #2, Run 220 .

DB-5, 30m x 0.5mm o.d., 65-290°C, 5°C/min.

Fig.7.12. GC analysis of aqueous liquor, catalytic hydropyrolysis, G33RS nickel catalyst, Coronach lignite #2, Run 226 .

DB-5, 30m x 0.5mm o.d., 65-290°C, 5°C/min.



7.4 PYROLYSIS OF $ZnCl_2$ IMPREGNATED LIGNITE

Various Lewis acids, particularly zinc chloride, has been reported to improve yields of tar from coal (24). $ZnCl_2$ is also inexpensive as an industrial catalyst. In an attempt to increase the yield of tar obtained from flash pyrolysis of lignite, Coronach lignite #3 was impregnated with zinc chloride. The method of impregnation of $ZnCl_2$ was adapted from the study performed by Kandiyoti et al. (25). The procedure is briefly described in an itemized form in the Appendix. The untreated and $ZnCl_2$ impregnated samples of Coronach lignite #3 were pyrolyzed in a sand fluidized bed at atmospheric pressure using a bench scale reactor.

Runs 230 and 231 were performed in N_2 with the original and $ZnCl_2$ impregnated lignites, respectively. Run 232 was done in H_2 with the $ZnCl_2$ impregnated sample. The effects of catalyst impregnation and pyrolysis atmosphere on the product distribution during the flash pyrolysis experiments are shown in Table 7.7.

Vapour residence times in the reactor were kept at 0.36-0.39s, because increases in vapour residence times are known to be detrimental to tar yields due to the secondary reaction of volatiles (8).

In the pyrolyses in N_2 at about 620°C, the tar yields were almost the same in both untreated and $ZnCl_2$ impregnated lignites, while the char yield observed in the pyrolysis of $ZnCl_2$ impreg-

Table 7.7. Pyrolysis of $ZnCl_2$ impregnated coal, bench scale unit, feed: Coronach lignite #3 (-250+74 μm), bed material: Ottawa sand (-590+300 μm).

Run	230	231	232
Atmosphere	N_2	N_2	H_2
Temperature (°C)	617	620	619
Vapour residence time (s)	0.36	0.37	0.39
Wt.of bed material (g)	60	60	60
Wt.of coal fed (g)	58.05	68.58	45.78
Moisture in feed (wt%)	21.71	12.76	12.76
Ash in feed (dry wt%)	16.21	16.21	16.21
$ZnCl_2$ (g/100g dry coal)	0.00	10.52	10.52
Product yields (wt % maf coal)			
Gas	22.47	21.94	26.40
Tar	16.26	15.96	15.98
Char	50.42	53.15	47.03
Water	10.29	8.80	5.35
Total	99.44	99.85	94.76
Gas yields (wt% maf coal)			
H2	0.18	0.75	ND
CO	5.10	5.81	8.90
CO2	14.31	12.89	13.06
CH4	1.89	1.31	2.42
C2H4	0.25	1.68	0.63
C2H6	0.18	0.10	0.21
C3	0.20	0.42	0.54
C4	0.18	0.37	0.27
BTX	0.17	0.12	0.36
Total	22.47	21.94	26.40

Note : ND = not determined.

nated lignite was higher than that of the untreated coal. This is a reversal of the char formation trend reported by Kandiyoti et al. (24). They observed lower char yields when pyrolyzing $ZnCl_2$ impregnated bituminous coal samples. The reversal in char production trends between Linby coal (a low rank, non caking British bituminous coal) and Coronach lignite #3 samples observed in flash pyrolysis under similar operating conditions might be due to the difference in the way $ZnCl_2$ catalyze the pyrolysis. It is possible that $ZnCl_2$, which has a low melting point (284°C), acts in an unique way depending on the petrographic structure of each parent coal. In view of the normal boiling point of zinc chloride (732°C), the vapour pressure of zinc chloride at 620°C would be relatively high. Therefore, lower temperature would be desirable in order to minimize the evaporation of zinc chloride.

From the results of analyses for gaseous products, it is indicated that $ZnCl_2$ catalyst can promote the carbon-steam reaction which produces H_2 and CO.

In Run 232 carried out in the presence of hydrogen, the gas yield markedly increased at the expense of water and char, leaving the tar yield virtually unchanged. The decrease in the water yield suggests that the re-routing of native hydrogen to favour hydrocarbon products is possible. The increase in the gas yield is due mainly to the increase in both H_2 and CO yields. It is also observed from Table 7.7 that CH_4 and BTX yields increased in

the presence of hydrogen. The decrease in C_2H_4 yield appears to be due in part to the hydrogenation of unsaturated bonds, and is not totally compensated for by the slight increase in C_2H_6 yield. Therefore, it is likely that the hydrocracking of C_2H_4, which can undergo C=C bond cleavage to yield CH_4, occurred.

Semi-quantitative analysis of tar products was carried out by means of high resolution gas chromatography. Conditions of GC analysis are the same as those described previously.

GC chromatograms of tars obtained from Runs 231 and 232 are shown in Figures 7.13 and 7.14, respectively. Concentrations of major compounds were determined in terms of CPA (Corrected Peak Area) for each component.

The results of a comparison between two atmospheres, i.e., nitrogen vs. hydrogen, are given in Table 7.8., together with those obtained from previous experiments without catalyst under otherwise comparable conditions.

Comparing the results of the uncatalyzed runs, it can be seen that hydrogen atmosphere reduces the concentrations of benzenediols, such as catechols and resorcinol, and slightly increases those of phenol and phenol derivatives. This trend appears to become less significant in the presence of $ZnCl_2$ catalyst except for the concentrations of phenol and catechol. As shown in Figures 7.13 and 7.14 and Table 7.8, benzene(B), toluene(T) and xylene(X) were identified using the same method described in

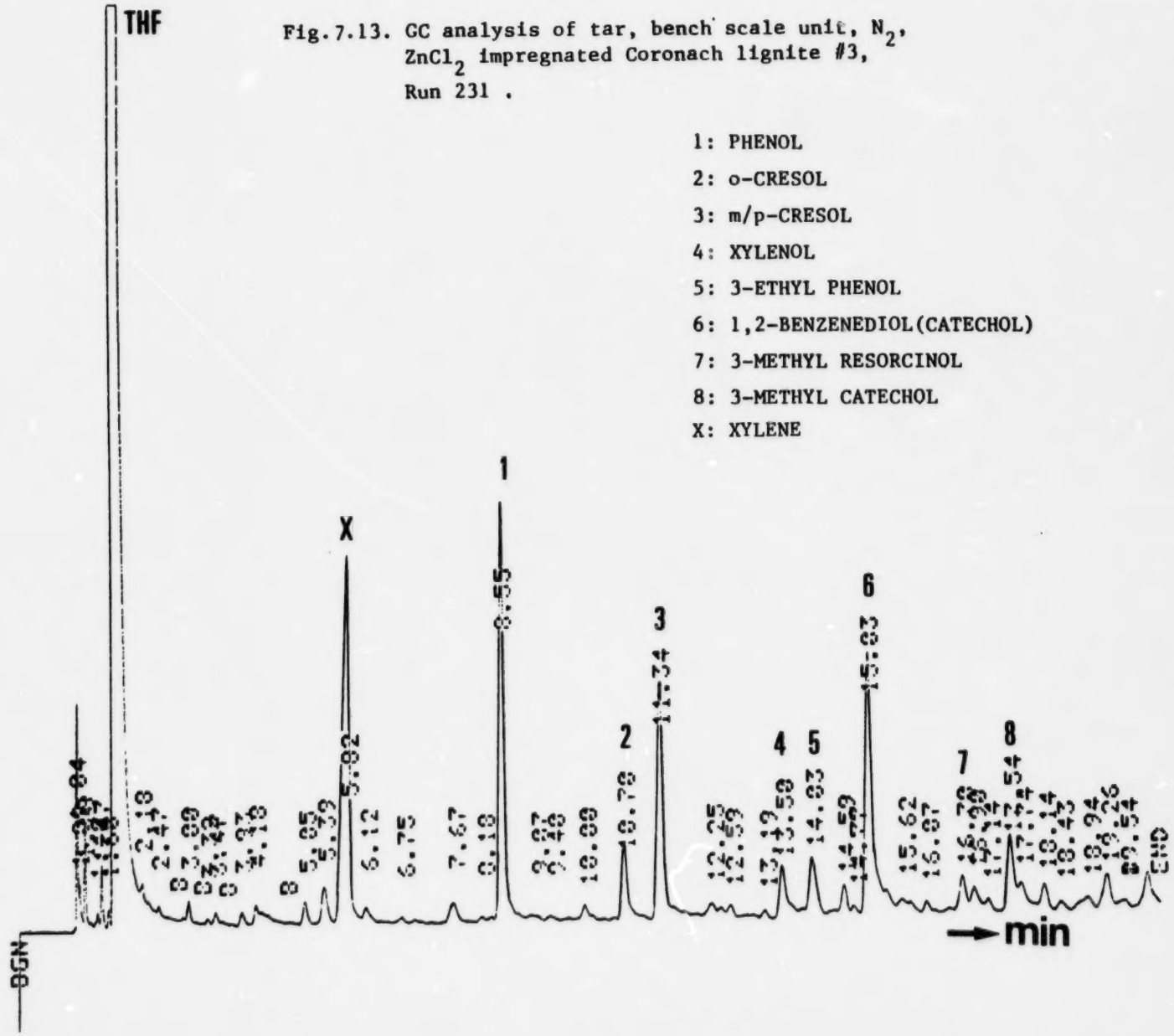


Fig.7.13. GC analysis of tar, bench scale unit, N_2, $ZnCl_2$ impregnated Coronach lignite #3, Run 231 .

1: PHENOL
2: o-CRESOL
3: m/p-CRESOL
4: XYLENOL
5: 3-ETHYL PHENOL
6: 1,2-BENZENEDIOL(CATECHOL)
7: 3-METHYL RESORCINOL
8: 3-METHYL CATECHOL
X: XYLENE

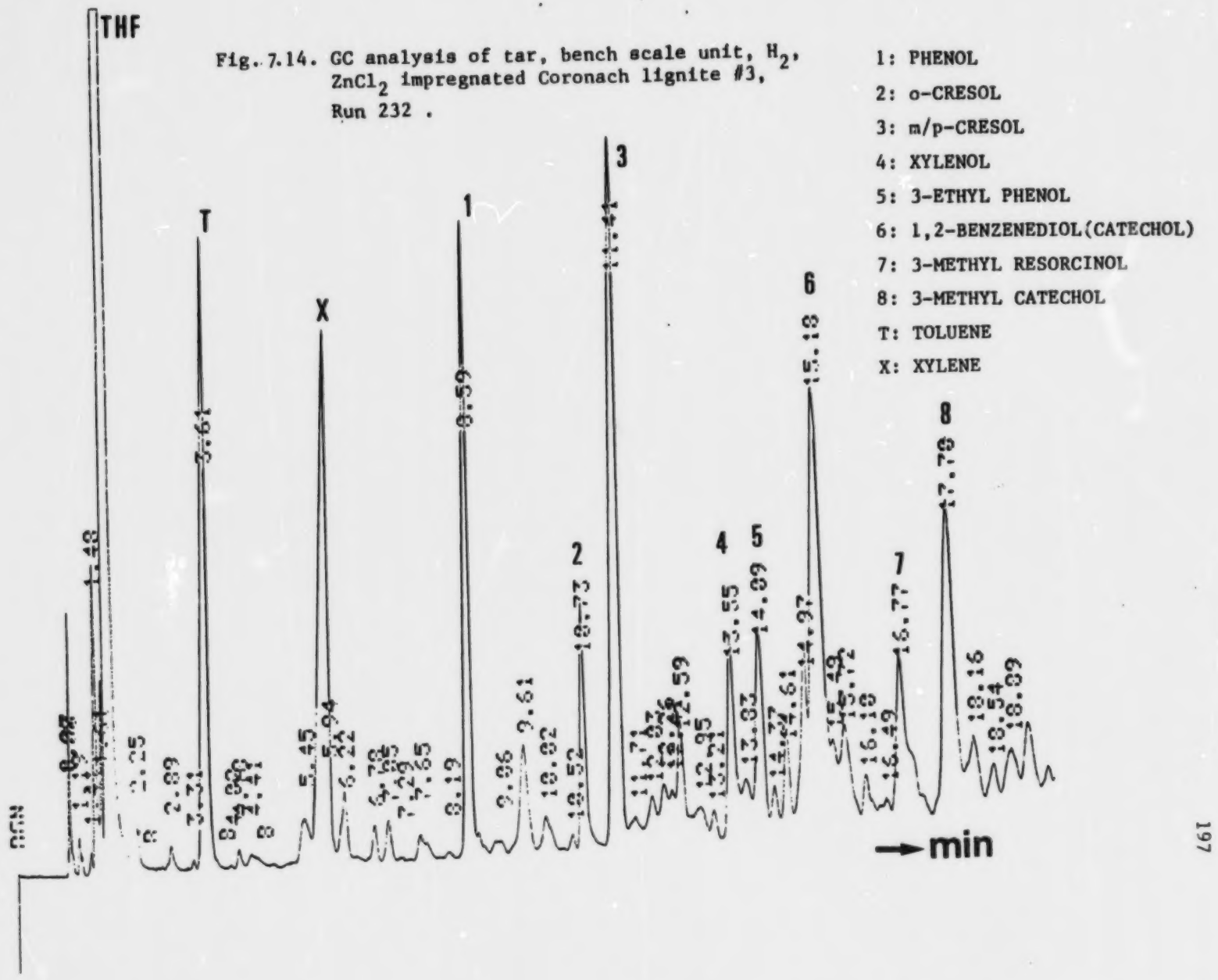


Fig. 7.14. GC analysis of tar, bench scale unit, H_2, $ZnCl_2$ impregnated Coronach lignite #3, Run 232 .

Table 7.8. Effect of $ZnCl_2$ impregnation on the composition of tar products from flash pyrolysis of Coronach lignites.

Run	231	232	P-79	215
Atmosphere	N_2	H_2	N_2	H_2
Reactor type	bench	bench	pilot	bench
Coal	Cor.#3	Cor.#3	Cor.#2	Cor.#2
Temperature (°C)	620	619	653	663
$ZnCl_2$(g/100g dry coal)	10.52	10.52	0	0
	(Tar yield,wt% maf coal)xCPA/100			
Benzene	tr	tr	tr	tr
Toluene	tr	0.164	tr	0.031
Xylene	0.289	0.264	tr	0.095
Phenol	0.251	0.334	0.105	0.203
o-Cresol	0.058	0.059	0.034	0.064
m/p-Cresol	0.189	0.189	0.120	0.214
Xylenol	0.047	0.031	0.035	0.056
Ethyl phenol	0.057	0.038	0.035	0.064
Benzenediols				
1,2-	0.233	0.080	0.215	0.068
2-Methyl-1,3-	0.031	0.016	0.082	0.029
3-Methyl-1,2-	0.058	0.062	0.143	0.051
Total	1.213	1.238	0.768	0.875

Notes:

(1) Cor.#2 = Coronach lignite #2
(2) Cor.#3 = Coronach lignite #3

(3) CPA(Corrected Peak Area) = $\frac{\text{FID peak area}}{\mu\text{l injected} - \mu\text{l of THF}} \times 0.2$

(4) tr = trace amounts

Table 6.5. The most distinctive feature of the composition of the $ZnCl_2$ tars is the high concentrations of BTX, particularly xylene under nitrogen atmosphere and both toluene and xylene under hydrogen atmosphere. No BTX is to be seen in the absence of both catalyst and hydrogen (see Table 7.8). This leads to the conclusion that the major catalytic activity of zinc chloride consists of the catalytic hydrogenation of reactive fragments formed by thermally induced bond cleavage, particularly phenols and benzenediols.

From literature (24) it is known that a systematically higher percentage of the hydrogen native to the coal mass was taken up by the tar product from pyrolysis under nitrogen atmosphere in the presence of zinc chloride than for the untreated coal. Based on the results shown in Table 7.8, this is to be interpreted as a deoxygenation reaction that can yield xylene from hydroxylated aromatic compounds in the absence of hydrogen.

On the other hand, $ZnCl_2$ is also known as one of the most effective hydrogenation catalysts. Results shown in Table 7.7 clearly demonstrate that Run 232 with $ZnCl_2$ under H_2 atmosphere resulted in the increase of the total conversion of gas and tar compared with Run 231 carried out in N_2. This is an indication that the $ZnCL_2$ catalyst has some effect on hydropyrolysis processes, namely the hydrocracking of coal structure bonds.

8. CONCLUSIONS AND RECOMMENDATIONS

PART A

8.1 CONCLUSIONS

The following conclusions can be drawn from the present study:

(1) Maximum tar yields of about 13% to 20% maf coal were obtained at about 650°C for all three coals, namely original and acid washed Coronach lignite #3, and Forestburg subbituminous coal. The maximum tar yields from the larger flash pyrolyzer (1-3 kg/h pilot plant unit) were identical or higher compared with those obtained with smaller bench scale reactors. At higher temperatures over 650°C tar yields decreased due to the secondary thermal decomposition accompanied by generation of gaseous products. In the results of solvent fractionation of tars, the effect of temperature on the yields of fractions was not necessarily the same for all coals tested. In general, the yields of solvent fractions were in the order asphaltene > oil > preasphaltene. Preasphaltene fractions contained substantial amounts (up to 2.9 wt% maf coal and up to 50% of the preasphaltene fraction) of methanol soluble fractions thought to be derived from the humic acid portion of lignites.

(2) The optimum feed rate to obtain the maximum tar yield appeared to exist at around 1.5kg/h. A higher feed rate of about

2.8kg/h resulted in a decreased tar yield accompanied by a higher yield of gaseous products. It is likely that the feed rate change may result in a temperature change inside the coal particles which would consequently affect the tar yield. In the results of solvent fractionation, oil yields were proportional to tar yields and therefore the highest oil yield was obtained at a feed rate of about 1.5kg/h.

(3) The tar yield obtained at a shorter residence time of 0.35s was almost the same as that of a residence time of 0.44s. This shorter residence time operation resulted in an elutriation of sand particles. Tars obtained under both the short residence time and the usual residence time were very similar in the yields of the oil, asphaltene and preasphaltene fractions. Therefore the effect of residence time ranging between 0.35s and 0.44s was not very significant in terms of yields and the solvent fractionation of pyrolysis liquid products.

(4) Coronach lignite #2 with a high moisture content of 9.59 wt% gave a higher tar yield (15.10 wt% vs. 13.59 wt% maf coal) compared with a low moisture content counterpart. Furthermore, Coronach lignite #3 with a much higher moisture content of 22.77 wt% gave a surprisingly high tar yield (17.32 wt% maf coal) and this tar yield was one of the highest yields obtained from Coronach lignite. The observed effect of moisture content , which warrants further study, suggests that there is a possibility of moisture being trapped in the pore

structure until temperatures as high as 650°C are reached and thus participating in the pyrolysis process. In the results of solvent fractionation, asphaltene and preasphaltene yields were proportional to the moisture content of coal while oil yields appeared to present no significant tendencies with respect to the moisture content.

(5) Forestburg subbituminous coal gave a tar yield similar to Coronach lignite #3 (17.21 wt% vs. 17.32 wt% maf coal) at about 650°C. These two coals had quite similar elemental compositions but were considerably different in their proximate analyses, especially in the ash contents (16.21 dry wt% with Coronach lignite #3 vs. 8.60 dry wt% with Forestburg subbituminous coal). Preasphaltene amounts from the solvent fractionation of Forestburg subbituminous coal pyrolysis tar were much lower than those from Coronach lignite #3, in particular at about 650°C. In the results of GC/MS analysis of toluene soluble fractions, the concentrations of catechol (1,2-benzenediol) and its derivatives from Forestburg subbituminous coal were lower than those from Coronach lignite #3. The difference in the tar compositions appears to reflect some differences in parental structures of these low rank coals.

(6) Coronach lignite #3 had a higher ash content compared with Estevan lignite #4 which was previously investigated by Scott (9). The exchangeable cation content of Coronach lignite #3

was approximately two times higher than that of Estevan lignite #4 except for Na. The major effect of acid washing of Coronach lignite #3 was the increase in tar yield (19.95 wt% vs. 17.32 wt% maf coal) with a parallel reduction of gas yield, mostly due to a decrease in CO_2 yield. In the results of solvent fractionation the acid washed Coronach lignite #3 always gave higher asphaltene yields than the parent lignite at temperatures tested. Thus it can be concluded that the increasing tar yields of acid washed Coronach lignite #3 are primarily due to the increase in the yields of asphaltene fractions. The GC/MS analysis of toluene soluble fractions, showed that the concentrations of catechol and its derivatives increased considerably when pyrolyzing the acid washed Coronach lignite #3, while the concentrations of phenol and its derivatives were comparatively unaffected by the acid washing pretreatment.

(7) A pentane soluble fraction from the pyrolysis tar obtained from Coronach lignite #2 was analyzed using GC/MS. The pentane soluble fraction contained considerable amounts of phenol derivatives, alkanes and alkenes from C_{14} to C_{26}. A toluene soluble fraction was also analyzed using GC/MS under the same conditions. The toluene soluble fraction obtained from Coronach lignite #2 tar contained substantial amounts of oxygenated aromatic compounds, such as phenols, cresols, xylenol, catechols and resorcinol.

(8) A tar from Coronach lignite #3 was subjected to thermogravimetric analysis in nitrogen at a heating rate of 100°C/min. The maximum rate of devolatilization was attained between 200°C and 300°C. The fraction with a boiling range between 200°C and 300°C generally corresponds to petroleum-originated kerosene and diesel fuel. It is interesting to note that the normal boiling points of major compounds found in coal pyrolysis liquids are mainly included in the temperature interval between 200°C and 300°C and thus potentially can be converted to alternative synthetic transportation fuel.

(9) Pyrolytic water yields from low rank coals were in the order Forestburg subbituminous coal > original Coronach lignite #3 > acid washed Coronach lignite #3 at about 650°C. Tar yields of these coals were in the reverse order. Therefore it is likely that yields of tar rise at the expense of water in pyrolysis of these low rank coals. Three organic compounds, namely phenol, cresol and catechol were separated from the aqueous product and identified using GC/MS. Phenol was found to be the most abundant component out of the three compounds present in the aqueous liquor.

(10) Most of the carbon was converted to char and the carbon conversion to char increased in general with decreasing temperature. From 20% to 35% of the hydrogen was converted to tar and the hydrogen conversion to tar is almost the same as that

to water. Only 5% to 13% of the original oxygen content was contained in the tar and the rest was rejected as gas, char and water. From 20% to 40% of the oxygen was converted to water at the expense of the hydrogen and the loss of hydrogen as water reached 16% to 33% of hydrogen present in the original coal.

(11) The carbon content of pyrolysis products increased with temperature in all cases. The hydrogen content of the tars generally decreased with temperature, except for the results obtained at about 550°C. The carbon content of the tars and gases was not significantly affected by coal type, by acid washing and by pyrolysis temperature. In contrast, the hydrogen content of the tars and gases is fairly dependent on the coal type and acid washing pretreatment. The H/C ratio of tars decreased steadily with temperature in all cases. The H/C ratios of tars were in the order Forestburg subbituminous coal > original Coronach lignite #3 > acid washed Coronach lignite #3. A hydrogen-rich tar in terms of the H/C ratio can be produced at specific operating conditions, such as lower temperature, shorter residence time and higher feed rate.

(12) The hydrogen contents of the oil and asphaltene fractions decreased with temperature while that of the preasphaltene fraction appears to be temperature independent. The carbon content of each fraction increased with increasing temperature. The oil fraction was found to have the highest carbon

content of three solvent fractions at all temperatures tested. The H/C ratio increased almost equally in all fractions when adding THF into the reactor. The present data on the addition of THF imply that THF becomes highly reactive under the pyrolysis conditions and thus generates hydrogen-rich reaction products.

(13) The contents of carbon and hydrogen of both the methanol soluble and insoluble parts of the preasphaltene fraction were nearly temperature independent. This result is consistent with that for the overall preasphaltene fraction, which did not present any trend in C and H content with temperature. The methanol-soluble fraction had a higher H/C ratio than did the methanol-insoluble fraction at temperatures tested. The low H/C ratios less than 1.0 generally correspond to polycyclic aromatic compounds, which may imply that the preasphaltene fraction consists mainly of polycyclic aromatic compounds and their oxygenated derivatives.

(14) Pyrolysis of Coronach lignite under H_2 produced more gas, less tar and less char when compared with the pyrolysis performed under N_2. A H_2 atmosphere promoted CO production and decreased CO_2 production. C_1 to C_4 hydrocarbons obtained from hydropyrolysis of lignite were essentially the same compared with those from pyrolysis under N_2. The effect of sand size on product yields from hydropyrolysis appears to be less significant than the other process variables.

(15) There exists a significant difference in tar composition between the two atmospheres: nitrogen and hydrogen. Phenol and m-/p-cresol were present in significantly greater quantities in the hydropyrolysis tars. In contrast, catechols decreased markedly in hydropyrolysis. The altered tar composition in hydropyrolysis reconfirms the possibility suggested by other researchers that basic differences in reaction mechanisms exist in the two atmospheres. The overall composition of organic compounds present in aqueous liquor was similar in general to that found for hydropyrolysis tar. The major components were phenol and cresols.

(16) The Ni catalyst resulted in only a minor change in char yield compared to the result of hydropyrolysis with sand in the bed. However, in the presence of catalyst as the fluid-bed medium, tar yields decreased remarkably. The yield of CO_2 with the nickel catalyst was lower than that with the sand and contrarily the yield of CO was slightly higher. The use of the Ni catalyst as a fluidizing solid slightly increased methane yield and BTX yield.

(17) The nickel catalyst caused hydrogenation of dihydroxybenzenes, such as catechol and resorcinol, but the effect of this catalyst on hydrogenation of monohydroxybenzenes, such as phenol, cresol and xylenol, was less significant.

(18) Hydropyrolysis of $ZnCl_2$ impregnated Coronach lignite #3 resulted in some increase in the total conversion compared with the pyrolysis performed in N_2. The most distinctive feature of the $ZnCl_2$ tars was the high concentrations of BTX, in particular xylene under N_2 atmosphere and both toluene and xylene under H_2 atmosphere.

8.2 RECOMMENDATIONS

Based on the results of the present investigation, the following recommendations are made:

(1) The benefits of addition of THF or of other similar compounds into the reactor as a way of maximizing tar yield and at the same time improving the tar quality should be investigated.

(2) The effect of natural moisture on coal pyrolysis should be investigated to determine the optimum degree of dryness of a lignite at which the maximum tar yield can be attained.

(3) The effect of the macrostructure of coal on its reactivity in pyrolysis reactions should be investigated in relation to the measurement of molecular weight reduction, which might be achieved through depolymerization reactions and subsequent mass transport processes.

(4) Vacuum drying of lignite has been reported as having profound effects on the chemical and physical behaviour of the dried lignite. The effect of the vacuum drying of lignite on the tar yield in high heating rate pyrolysis should be investigated in order to relate the changes observed in pore structures to the subsequent changes in the reactivity of the lignite.

(5) A hydropyrolysis test should be carried out at atmospheric pressure in the large Waterloo flash pyrolysis reactor (1-3kg/h pilot plant unit), operated as a catalytic hydropyrolyzer.

(6) The performance of gel permeation chromatography (GPC) to separate the low molecular weight components from high molecular weight molecules prior to the detailed characterization by GC/MS should be evaluated, particularly for coal-derived tars containing substantial amounts of asphaltene and preasphaltene fractions.

(7) The performance of absorption spectrometry in the visible and near ultraviolet regions to determine aromatic ring structures of polycyclic aromatic compounds should be evaluated for asphaltene and preasphaltene fractions of coal liquids.

(8) Several Lewis acid catalysts, such as the chlorides of zinc, tin and aluminum, have been reported to improve yields of condensible liquids from coal. Possible improvement in the yield and nature of tar products should be investigated in more detail using Lewis acids as the catalyst, with which lignite is impregnated prior to flash pyrolysis.

RESULTS AND DISCUSSION

PART B

9. PYROLYSIS OF COPROCESSING RESIDUES

9.1 INTRODUCTION

At the present time, CANMET has under development an upgrading process in which mixtures of coal and bitumen or heavy residue are subjected to liquefaction at high temperatures and pressures. There is evidence of a synergistic effect in such coal-bitumen mixtures which results in enhanced yields of motor grade fuels. Depending on the feed materials and the reaction conditions used, some residue always remains after product distillation is completed. Even if this residue amounts to only 10% to 20% of the feed, it represents a large amount of presently unusable product when the probable scale of a commercial upgrading plant is considered. Indeed, all upgrading processes for bitumen, heavy residues or coal will produce varying amounts of this refractory end product. At the present time, the only apparent use for this material is as a low grade fuel, or as a feed for a gasification process. If the sulfur and nitrogen contents are high, it may not even be desirable to use it for these purposes. Alternative processing or uses for these residues from upgrading processes therefore are needed to assist in making various upgrading technologies more attractive both technically and economically.

One possible alternative technology for residues, including that from coprocessing, would be a fast pyrolysis process which would recover additional light hydrocarbon liquids and gases and a dry coke having good physical properties and a reasonably good reactivity, which might be useable as a fuel, or which could be safely stock-piled. Preliminary tests using thermal gravimetric analysis (TGA) indicated that significant yields of volatiles could be obtained from the CANMET coprocessing residue using rapid pyrolysis. More detailed investigations of atmospheric flash pyrolysis were therefore proposed using the fluidized bed technology developed as the Waterloo Fast Pyrolysis Process for coal and biomass.

Major problems in pyrolyzing these materials were anticipated because of the nature of the coprocessing residues (which are shared with most upgrading residues). The residue feed can range from tarry liquid to a dry granular form - the latter is more typical of CANMET coprocessing residues. However, on heating all these materials pass through a sticky, plastic stage and at higher temperatures decompose to form volatile products and coke. Because the precursor stage to coke formation is sticky, the residue adheres to surfaces, and the coke then forms at these surfaces as temperature increases. These two factors require some special operating and constructional features in any pyrolysis reactor. The sticky phase can cause severe problems in feeding the residue to a hot reactor zone, and the deposition of coke on

reactor surfaces can lead to reactor shut-down. These problems are magnified in small scale laboratory continuous flow reactors.

Much of the work reported in this section describes the attempts made during the contract period to devise a continuous flow fast pyrolysis reactor capable of handling these difficult feed materials in a simple and economical process, while at the same time producing light hydrocarbon liquids and gases, and a dry coke residue which could be recovered in a useable form. Because of the sequential nature of the tests, some of the work carried out is presented chronologically rather than in more conventional categories.

9.2 MATERIALS AND APPARATUS

9.2.1 Materials Used

One serious problem existed from the outset in evaluating the pyrolysis behaviour of CANMET coprocessing residues. Because these were produced in a small-scale pilot plant, only limited quantities were available for a given set of test conditions. Therefore, much of the "learning" period, as well as preliminary experimentation with novel reactor designs, had to be carried out with substitute materials which would simulate coprocessing residue behaviour. Two such materials were used; a heavy vacuum bottoms residue from the Suncor refinery in Sarnia, Ontario, and a bituminous caking coal (Balmer) from British Columbia.

Details of the reactions conditions under which coprocessing residues were produced is proprietary. These residues are identified, therefore, by a code number only. Similarly, detailed information from Suncor concerning the feedstock source of the vacuum residue sample was not available.

Figure 9.1 shows the results from the thermal gravimetric analysis of the two coprocessing residue samples received from CANMET. Both of these were very similar in appearance, as brown granular powders (SF 181085-1, -2). The samples were heated in nitrogen from an initial temperature of 100°C and increasing at 100°C/min to a final temperature of 950°C where they were held for 1.5 minutes. The results illustrate the volatile content only and show clearly that there is very little difference between the two samples in this respect. Volatiles contents were 50 and 55 percent for samples SF 181085-1 and SF 181085-2, respectively. Most of the volatiles appear to be removed below 600°C, suggesting that lower pyrolysis temperatures should perhaps be investigated. In fact, this residue has been vacuum distilled and is classed as a +525°C material.

Table 9.1 shows the ultimate analysis of two coprocessing residues produced from the CANMET coprocessing unit. One of the residues (SF 181085-2) was extracted for about four hours in THF using a Soxhlet extraction apparatus. The THF insoluble fraction was 20 percent by weight of the total residue. The ultimate analysis of this fraction is also given in Table 9.1. This THF

Figure 9.1: TGA Volatile Determination of Coprocessing Residues

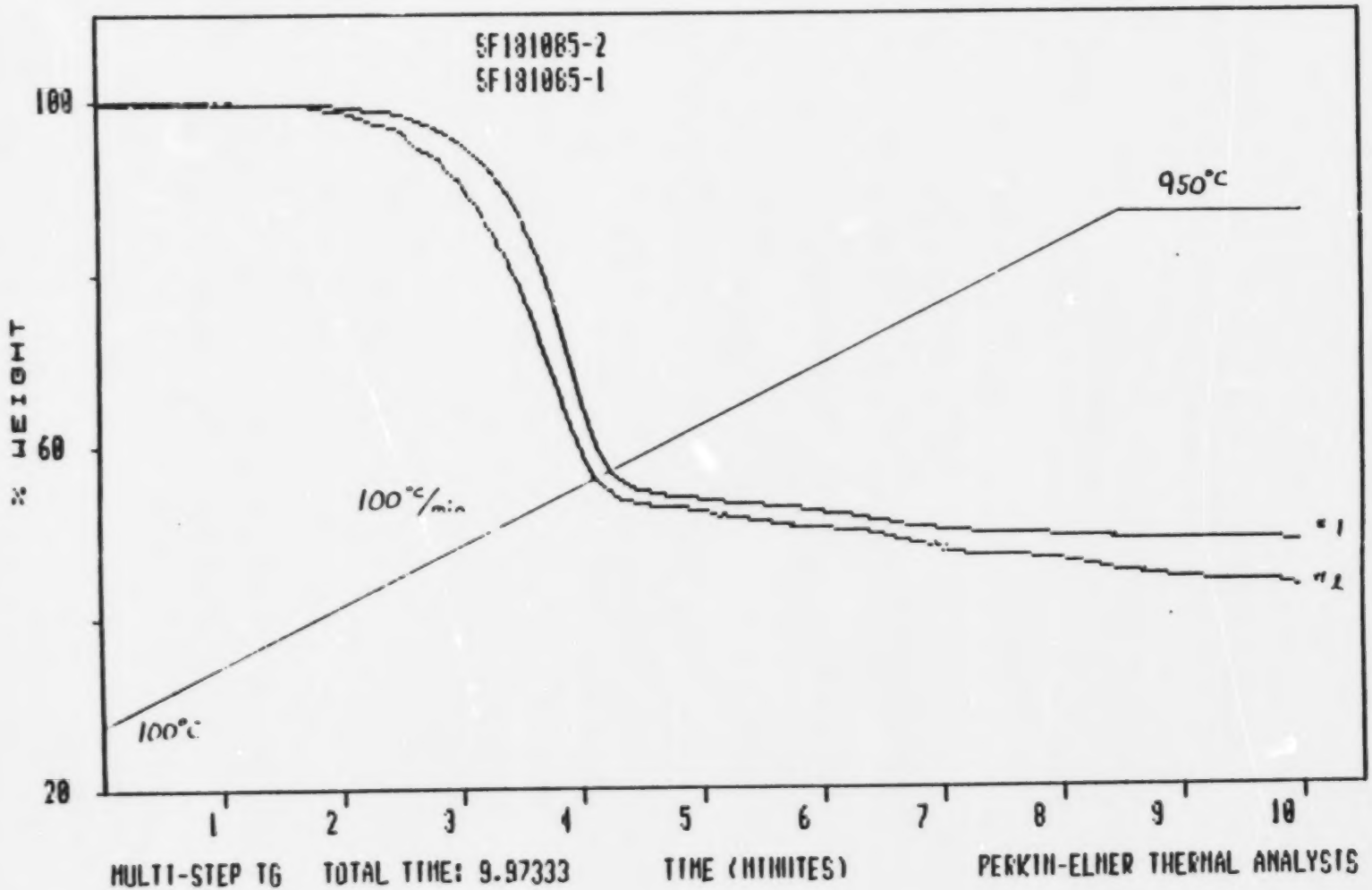


Table 9.1

ANALYSES OF COPROCESSING RESIDUES

ULTIMATE ANALYSIS

wt % as is (maf)

	C	H	N	S	O (by diff)	Ash
SF 181085-1	71.70,76.0*	5.95,6.61*	0.94,1.39*	5.16*	5.2,3.0*	11.0*
SF 181085-2	72.02,74.3* (82.01)	5.94,6.16* (6.76)	1.39,1.30* (1.58)	5.15*	3.3,3.2*	12.18 13.5*
SF 181085-2** THF Insoluble	24.54 (62.76)	1.38 (3.53)	0.33 (0.84)			

* Values from CANMET

** maf values calculated assuming all ash in THF insoluble fraction

insoluble residue is markedly lower in its carbon, hydrogen and nitrogen contents than the whole residue indicating that this fraction is rich in inorganic matter originating from the coprocessing feedstock and/or the CANMET additive.

Table 9.2 gives the proximate analysis of the two residue samples. The moisture and volatile fractions were determined from the TGA results given in Figure 9.1. The ash content was determined by combusting weighed samples (0.5 - 1.0 g) of residue at 950°C in air for two hours. Fixed carbon was determined by difference.

The vacuum bottoms residue was obtained from Suncor in December, 1985. No information was supplied with this sample except that it was a boiling range 400°-565°C fraction. However, as this material was used only for learning and simulation tests, its exact composition was of minor interest. It showed strong coking tendencies when heated, and was a black solid at room temperature, typical of this type of residue.

The proximate and ultimate analyses of Balmer bituminous coal are given in Table 9.3. This coal has a moderate swelling index of 4.0, and was used to test reactor designs which might minimize the accretion of coke or of agglomeration within the reactor.

Table 9.2

COPROCESSING RESIDUE

PROXIMATE ANALYSIS

wt % as is

	Moisture	Volatiles	Fixed Carbon	Ash
SF 181085-1	0	52.2		
SF 181085-2	0	56.7	31.12	12.18

Table 9.3

ANALYSES OF BALMER BITUMINOUS COAL

Proximate Analysis, Wt %

	As-Is	maf
Ash	9.78	
Moisture	0.64	
Fixed Carbon	69.71	77.82
Volatile Matter	19.87	22.18
FSI	4.0	

Ultimate Analysis, Wt %, maf

	CANMET	Waterloo
Carbon	90.36	89.08
Hydrogen	4.79	4.28
Sulfur	0.30	ND
Nitrogen	1.26	1.45
Oxygen (by difference)	3.29	5.19
H/C Molar Ratio	0.64	0.58

9.2.2 Apparatus and Procedures

Initial tests were carried out in the bench scale fluidized bed apparatus, which has been described in detail in previous reports (9). However, because it was planned to carry out pyrolysis tests to higher temperatures than used previously for coal, that is, above 750°C, the stainless steel reactor normally used would not be adequate. Therefore, a new reactor was constructed which was a duplicate of the existing bench scale unit but made of a high temperature alloy. This new reactor was made of Inconel 601, and had an inside diameter of 25.4 mm (1 inch). Details and dimensions are shown in Figure 9.2a. Both this reactor and the usual stainless steel reactors were used in the various pyrolysis tests carried out, depending on the temperature level employed.

Analytical methods used to measure char, liquid products and gases were identical to those used for bench scale coal pyrolysis tests described in Part A, and also described in earlier reports (9). Solvent fractionation of pyrolysis tars was identical to the procedure used for coal tars described in Part A.

9.3 PRELIMINARY FEEDING TESTS

A preliminary test with the normal feeding system and feed injection into the fluidized bed showed that the coprocessing material became liquid when warmed and could decompose in the inlet feed tube. Therefore, a series of tests was done to develop

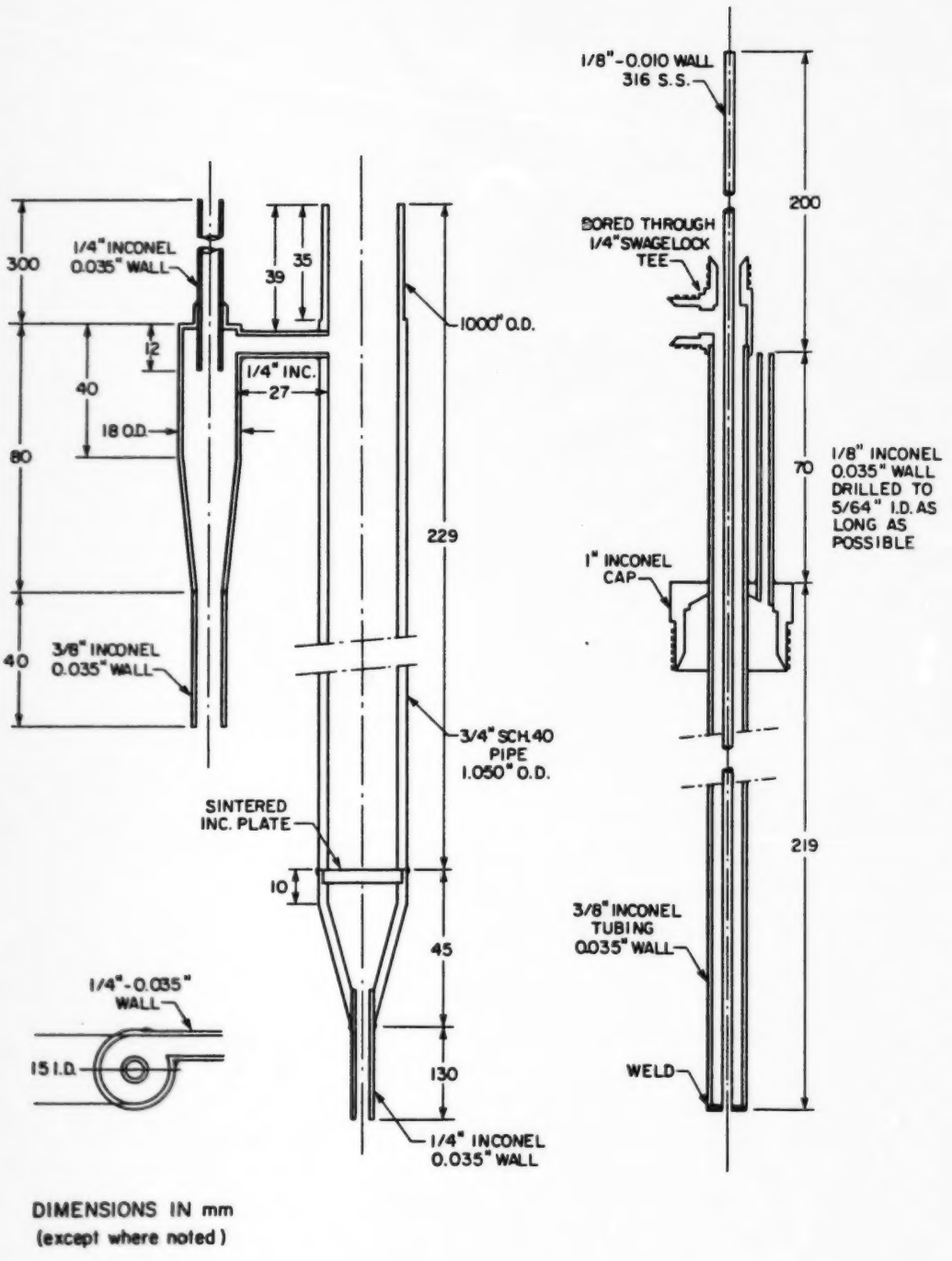


Figure 9.2a Details of Inconel Bench Scale Reactor

a liquid feeder for the fluid bed pyrolysis unit.

The initial liquid feeder constructed and tested was intended to allow feeding of flowable residues. It was of the piston-style batch type using gas pressure as the force to cause flow, with a fixed capillary resistance to control feed rates to about 60 grams per hour, at temperatures to 150°C. The heavy vacuum bottom residue from Sun Oil was used as a test material. The feeding device was held in a small single zone furnace 30 cm long by 7.5 cm diameter with 1400 W input. The temperature of this furnace was normally controlled at about 150°C.

A capillary tube, 0.020 inch I.D. (0.51 mm), was used to increase the pressure drop of the liquid and give greater flow control. The feeding vessel was suspended in an electrically heated furnace maintained at 150°C. The hot liquid was forced up the capillary tube and through a 1/8 inch O.D. tube with a 0.010 inch wall (2.67 mm I.D.) heated with an electrical tape controlled by a variable voltage supply. The 1/8 inch O.D. transfer tube was connected to the air cooled 1/8 inch O.D. injection tube of the reactor. The liquid was thus forced through the tubes into the fluidized bed of sand. This feeding system, however, resulted in very unsteady feeding and eventual (~34 min.) plugging of the injection tube. Evidently, for a bed temperature of 700°C the injection tube could not be cooled sufficiently by the air jacket to prevent coking of the feed in the tube. This insufficient

cooling and the long transit time of the feed in the tube (about 30 seconds) combined to cause the plugging of the tube due to coke formation.

Tests showed that if additional cooling was provided for the feeding tube the fluidized bed itself could not be maintained at reaction temperature (700°C). A smaller injection tube, 1/16 inch O.D. with a 0.009 inch wall thickness (1.13 mm I.D.) was inserted to decrease the transit time of the feed in an attempt to inject the feed to the bed before coking could occur. This resulted in steadier feed rates but earlier plugging (13 minutes) of the injection tube.

An even smaller injection tube, 0.042 inch O.D. with 0.007 inch wall thickness (0.71 mm I.D.), was inserted and a 500 ml/minute (20°C - 1 atm) flow of nitrogen in the annulus between the 1/8 inch O.D. reactor feed injection tube and the 0.042 inch O.D. injection tube provided some additional cooling. This scheme resulted in plugging of the very narrow injection tube after only 2 minutes.

To speed the flow of the liquid feed through the injection tube, the feeder was modified to cause the hot liquid to be entrained in a stream of nitrogen. This design is very similar to the Scott feeder for solids. A U-tube with a 0.026 inch (0.66 mm) diameter hole at the lowest point was inserted into the sealed vessel. Pressure was applied to the vessel (from 5 to 30 psi) and

a flow of nitrogen (500 ml/min) through the U-tube entrained some liquid and carried it through the injection tube. Calibration tests showed feeding to be very erratic with occasional plugging, and therefore a pyrolysis run was never attempted.

Another scheme, shown in Figure 9.2b, replaced the U-tube with an open-ended capillary tube submerged in the feed liquid with gas pressure forcing the liquid through the tube to the injection tube as before. However, at the top of the injection tube the hot liquid was entrained in a nitrogen stream (500 ml/min) and carried into the reactor. This method resulted in very steady feeding of approximately 20 g/h for about 15-20 minutes. However the injection tube plugged before more than 8 grams could be fed.

It was apparent that feeding these bitumen-like materials at a controlled rate on such a small scale was prone to many problems. However these initial tests showed that, with refinement of the above methods these problems should be minimized, and steady feeding for the time required for one run should be feasible.

9.4 PRELIMINARY PYROLYSIS TESTS - VACUUM BOTTOMS

Table 9.4 shows the results from two runs using vacuum tower bottoms. As noted in the Table, different feeders were used for each run. Run 204 used gas pressure only to force the liquid directly into the 1/8 inch O.D. injection tube. Run 206 used gas pressure to force the liquid to the top of the 1/8 inch O.D.

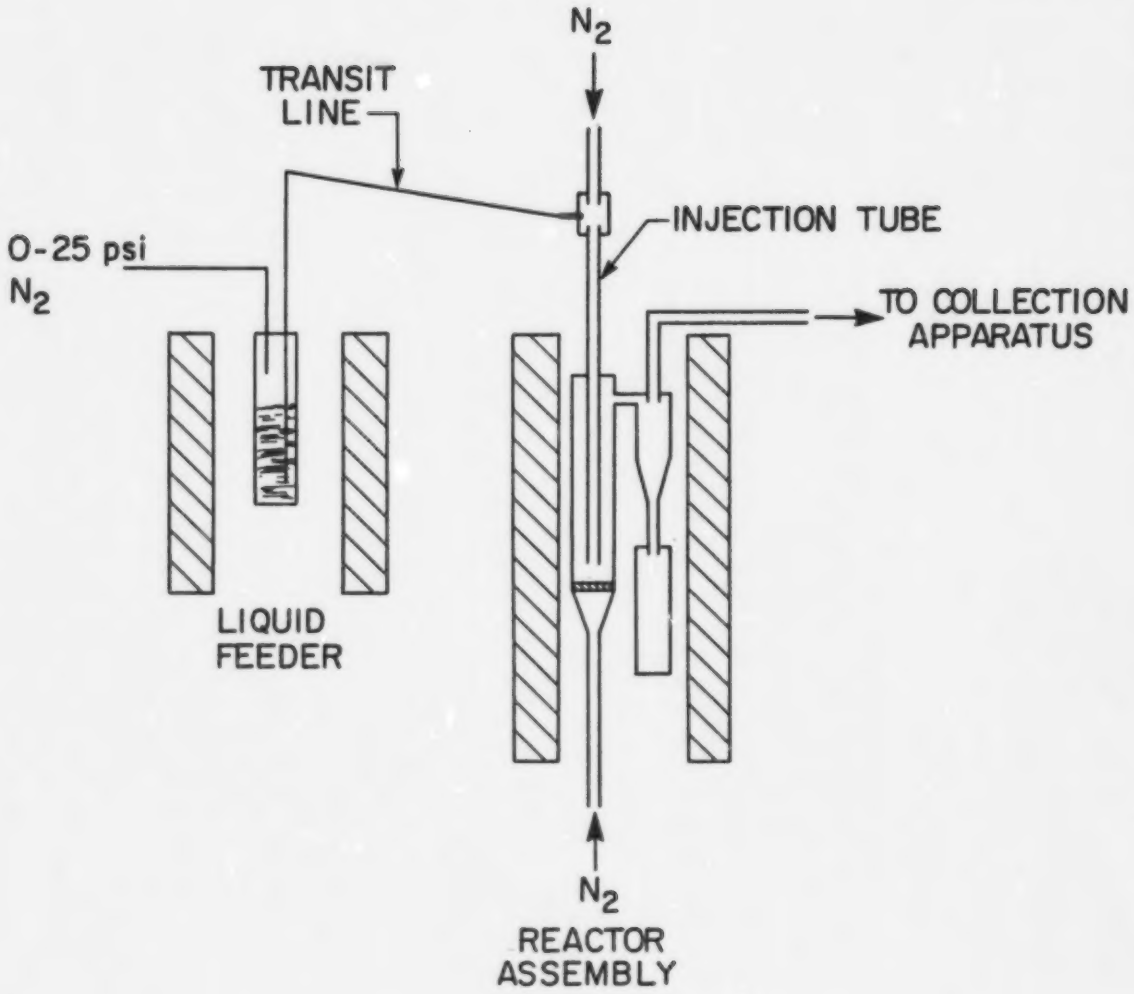


Figure 9.2b Liquid Feeder and Pyrolysis Reactor Assembly for Vacuum Tower Bottoms Residues

Table 9.4

Pyrolysis of Vacuum Tower Residue (Suncor, Sarnia)

Run No.	204*	206**
Temperature, °C	700	700
Sand Size, μm	-300 +250	-300 +250
Sand Amount, gms	25	25
Duration of Run, min.	34	23
Weight Fed, gms	7.67	7.39
Vapour Residence Time, secs.	0.45	0.45
Moisture in Feed, wt. %	N.D.	N.D.
Ash in Feed, dry wt. %	N.D.	N.D.
Yields, wt. % maf		
Gas	35.07	32.21
Tar	49.54	66.17
Char	26.73 [1]	2.43 [2]
Water	0	0
Total Recovery	111.34	100.81
Yields of Gases, wt. % maf		
H_2	0.39	0.41
CO	2.09	N.D.
CO_2	1.96	0.95
CH_4	4.82	3.79
C_2H_4	6.26	8.39
C_2H_6	1.96	1.35
C_3	5.48	5.95
C_4^+	12.13	11.37

N.D. Not Determined
* Used piston style feeder with 1/8" O.D. injection tube
** Used piston style feeder with nitrogen entrained injection tube
1. Residue remaining in reactor
2. THF insoluble residue in reactor

injection tube where it was entrained in a stream of nitrogen (see Figure 9.2b).

Gas yields for the two runs are very similar. However, char and tar yields differ significantly. This difference is due to different methods of collecting the products. For Run 204 the difference in weight of the reactor assembly before and after the run was assumed to be char only. For Run 206 the difference in the weight of the fluid bed was assumed to be char while the remaining weight difference of the reactor assembly was assumed to be condensed tar. In subsequent tests, the entire reactor assembly was washed in tetrahydrofuran (THF), and the washings filtered to obtain more accurate char and tar yields.

The gas yields shown in Table 9.4 show that both runs produced very little hydrogen and carbon oxides but relatively large quantities of methane and olefins. Because of the large amounts of C_4+ gases, these gases probably would be worth being more accurately identified and quantified.

The pyrolysis tar fog produced was very difficult to remove either by ice-water condensers or by an electrostatic precipitator, the latter probably because of the non-polar nature of the liquids. In both cases the downstream cotton wool filter collected a large fraction (about one third) of the liquid produced. Later runs employed glass wool as a filter which could be solvent washed to recover the tar.

Although detailed compositional analysis of the liquid product was not done, it was visibly different from the feed material. It was not as viscous as the feed and its colour was slightly lighter.

Figure 9.3 shows the analysis of a vacuum bottoms pyrolysis tar of Run 204. Although individual components have not been identified it is evident that decomposition to numerous lighter constituents has taken place. It was determined that the product liquid was considerably less viscous than the feed material. These preliminary results indicate that flash pyrolysis has the potential of producing 50-65% yields of lighter, more valuable liquid products from a vacuum tower residue as well as good yields of olefin gases.

9.5 ADDITIONAL FEEDING TESTS

Further modifications of the feeding procedure were devised in order to overcome the main problems for the liquid feeder of too long a transit time in the feed tube, and too much cooling effect on the reactor if the feed line were kept cool over its entire length. Also, because some of the coprocessing residue was a reasonably dry granular solid at room temperature, it could be fed with the normal solids feeder used for bench scale work if the feed line could be kept sufficiently cooled.

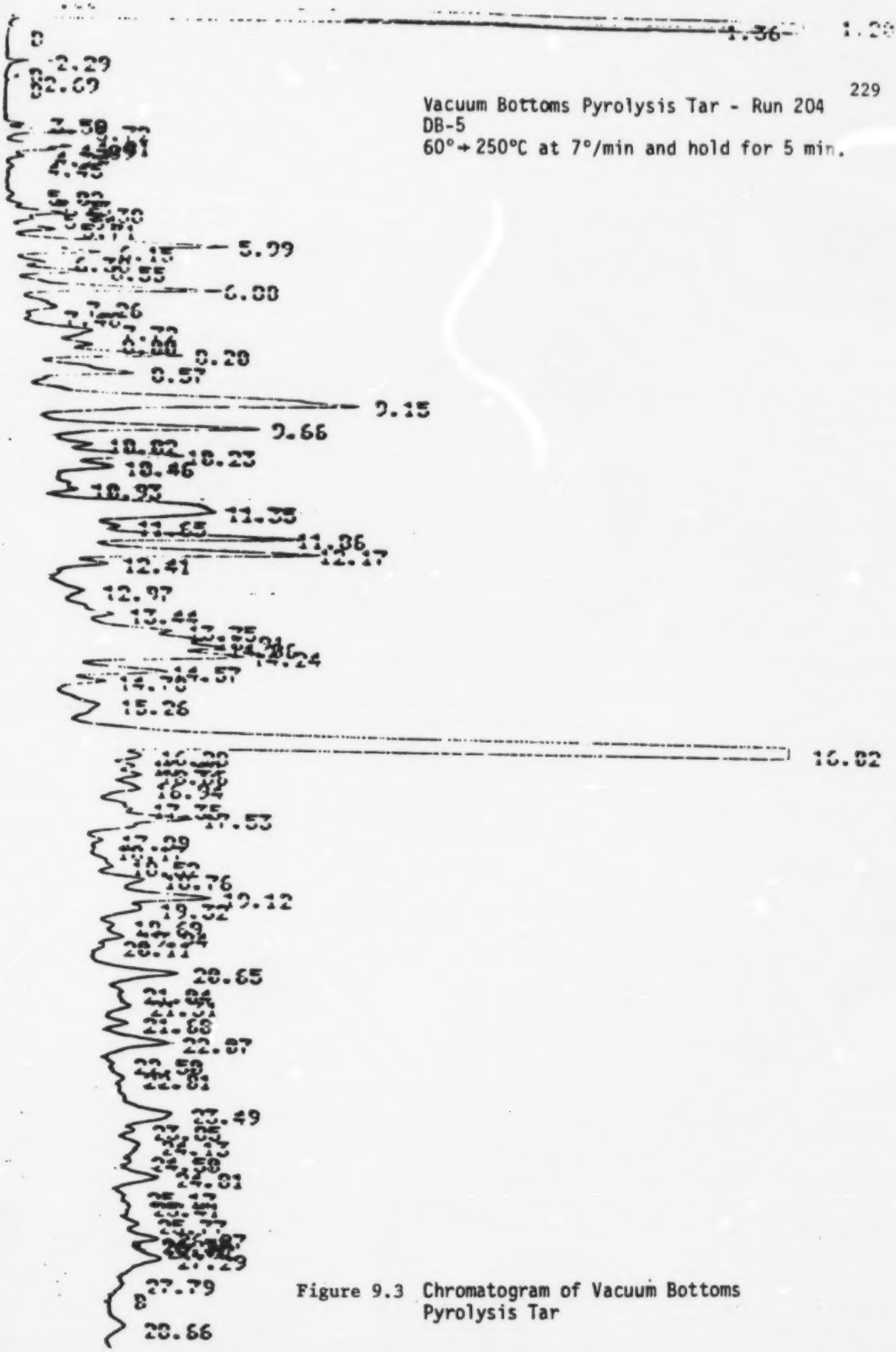


Figure 9.3 Chromatogram of Vacuum Bottoms Pyrolysis Tar

Numerous attempts were made therefore to feed vacuum tower bottoms and coprocessing residues into the hot fluidized bed without plugging the injection tube. Many tests were abandoned when the tube became blocked with either a viscous liquid, or a solid coke, or both. The injection tube was modified to allow better cooling of the tube while minimizing the cooling of the fluid bed. As shown in Figure 9.4, this was done by having the new injection tube run external to the reactor and introduce the feed material into the fluid bed at the reactor wall just above the porous plate. Cooling water was used to cool the feed tube but had a minimal effect on the bed with this external jacket.

The liquid feeder described in the previous section was modified slightly to improve its operation. An entrainment tube with a 0.33 mm diameter orifice was inserted vertically in the feeder (see Figure 9.4). The feeder was heated by an electrical heating tape and suspended above the reactor so that the length of the transit line was minimized. A stream of nitrogen, assisted by gravity, entrained the hot liquid down the entrainment tube into the injection tube.

Pyrolysis attempts with this apparatus resulted in an agglomerate of the sand and feed cementing the end of the injection tube. Only about 7 grams of vacuum bottoms could be fed before plugging stopped the run (about 15-20 minutes operation).

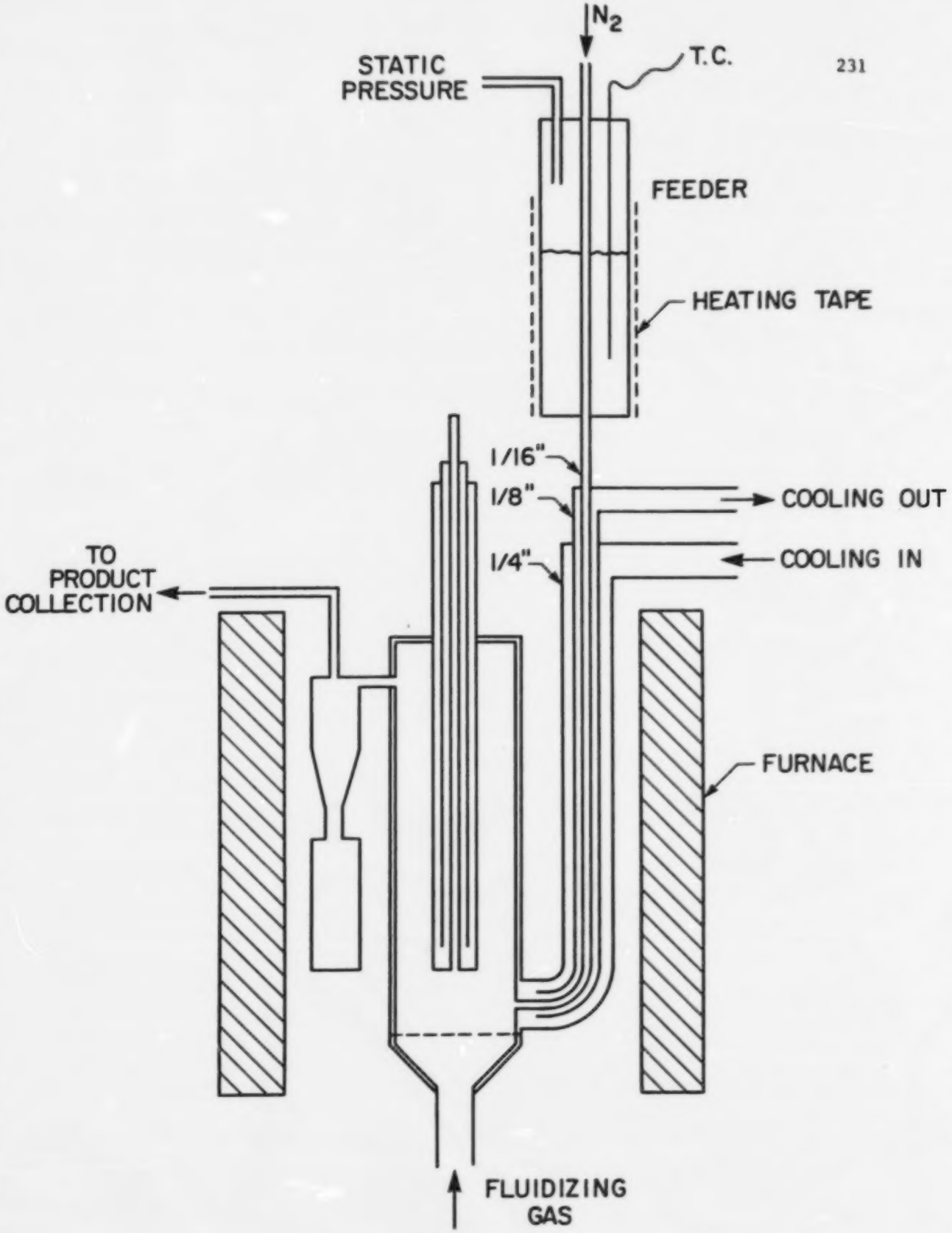


Figure 9.4 Modified Feed Arrangement for Bench Scale Fluidized Bed for Pyrolysis of Coprocessing Residues

A sample of coprocessing residue was ground to less than 250 μm. This material was fed to the feeder as a powder using a modified Scott solids feeder with a much lower solids holdup. Attempts to pyrolyse these residues at reactor temperatures of 700°C with the normal feed injection into the fluid sand bed resulted in plugging at the end of the injection tube with agglomerated sand and coke, which occurred regardless of the amount of cooling provided.

To avoid this plugging of the end of the injection tube, the larger (154 ml) stainless steel reactor was modified as shown in Figure 9.5. The centre injection tube was shortened so that the feed would enter the freeboard above the bed. This resulted in a mass of solid, porous coke filling the reactor for about 3.8 cm immediately below the injection tube (see Figure 9.5). The reactor plugged at the outlet after running for 28 minutes and feeding 18.9 grams. The gas yield for this run was only 4 percent compared with 20 percent for a run in which the feed was injected directly into the fluid bed, suggesting that the vapour residence time was extremely short, resulting in the evaporated light components exiting the reactor before any cracking could occur.

9.6 INITIAL PYROLYSIS TESTS - COPROCESSING RESIDUES

Results of pyrolysis runs using fluidized bed reactors with various feed arrangements are shown in Table 9.5. Plugging of the feed line and/or bed sand caused each run to be discontinued at

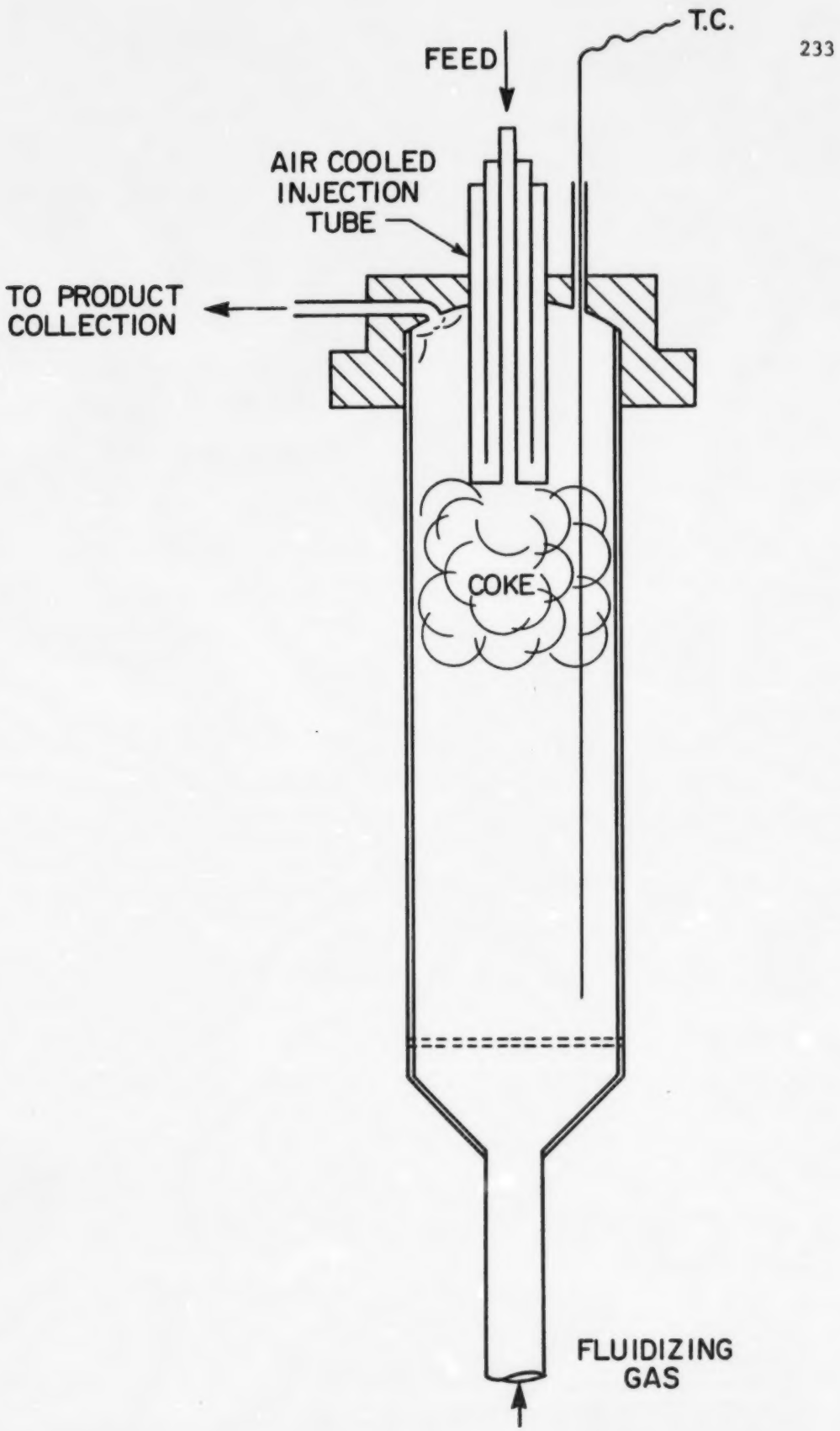


Figure 9.5 Modified Injection Tube Arrangement for Bench Scale Fluidized Bed Reactor for Pyrolysis of Coprocessing Residues

Table 9.5 PYROLYSIS OF COPROCESSING RESIDUES

Sample SF 181085-2

Run No. Feed	208 small inconel reactor	213 Top Feed large reactor	214 Bed Feed large reactor
Temperature, °C	675	700	535
Residue Size, µm	-250	-250	-250
Sand Size, µm	-590 + 300	-590 + 300	-590 + 300
Sand Amount, gms	25	60	60
Duration of Run, min	12	28.25	11.5
Wt. of Residue fed, gms	6.47	18.9	16.2
Vapour Residence Time, seconds	0.44	0.50	0.48
Moisture in Feed, wt.%	0	0	0
Ash in feed, dry wt.%	12.18	12.18	12.18
Yields wt.% maf			
Gas	32.67	6.00	2.67
Tar	N.D.	49.43*	40.07
Char	N.D.	44.57	47.98
Water	N.D.	0	0
Total Recovery		100.00	90.72
Yields of Gases, wt.% maf			
H_2	5.86	0.47	0.27
CO	6.33	0.0	0.28
CO_2	3.57	0.41	1.23
CH_4	3.54	1.48	0.09**
C_2H_4	3.42	0.58	0.05
C_2H_6	2.41	0.49	0.10
C_3	2.67	0.91	0.19
C_4^+	4.87	1.66	0.46

* calculated by difference
** Estimated

less than the normal run time of 30 minutes. Because of these operating problems some results were incomplete, and total recoveries were not good. However, the results do illustrate the potoential that flash pyrolysis holds for the cracking of these residues to lighter products.

The yields of pyrolysis gases for Run 208, using the small Inconel reactor with normal feed injection into the bed, are shown in Table 9.5, and demonstrate the relatively high yields of olefins and other light hydrocarbons obtained in combination with high hydrogen yields and low carbon oxide yields. These results were not duplicated in Run 213 in which the residue was fed into the freeboard of the fluidized bed and probably exited the reactor after a very short residence time, possibly without reaching the reactor temperature. As the results of Run 214 illustrate, in which normal feed injection as a solid into the bed was used, the production of gaseous products from this +525°C residue is very dependent on temperature. The low gas yield of Run 214 is not surprising considering that the low reactor temperature of 535°C is practically the same temperature as that of the process which produced the residues. The char yields of Runs 213 and 214 are very similar to the yields of fixed carbon plus ash determined by TGA results for the proximate analysis of the residue.

9.7 RESIDUE PYROLYSIS IN NOVEL REACTOR DESIGNS

9.7.1 Spouted Bed Reactor

Initial work focused on the design and testing of a new spouted bed reactor. Conceptually, the residues were to be entrained in the high velocity jet and carried up the central core of the bed. It was hoped that they would pass through the tacky liquid phase in this spout region and by the time they reached the fountain a solid non-sticky char would have formed which would fall back onto the annulus. When devolatilization was complete the char should be carried out of the reactor with the fluidizing gas.

A new spouted bed pyrolysis reactor was built and tested in an attempt to minimize the detrimental effects of swelling and agglomeration of the feed during fluidized bed pyrolysis. Several pyrolysis runs with the coprocessing residue were done with the new reactor. Results indicated that the spouted bed performed better than the fluidized bed when pyrolyzing caking materials. Solvent fractionation of the pyrolysis products was done. The major gaseous product was ethylene.

The spouted bed reactor apparatus is illustrated in Figure 9.6. The coprocessing feed was designed to be entrained as a powder in the gas stream and to enter the reactor in the spout. It was hoped that the high velocity (30 m/s) in the spout inlet would prevent agglomerates from plugging the inlet and would also

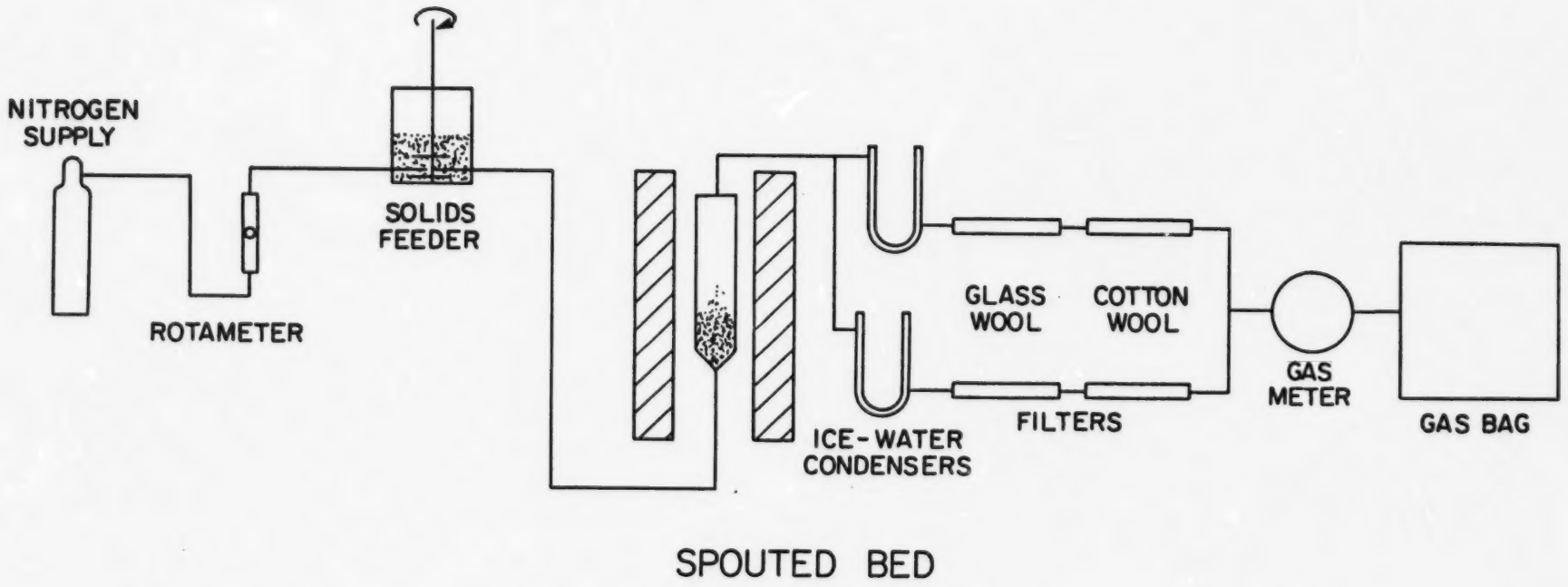


Figure 9.6 Schematic of Bench Scale Spouted Bed Pyrolysis System for Coprocessing Residues

prevent agglomerates from forming in the spout. The slower moving annular region of the bed might then be a more likely area for agglomeration to occur.

Pyrolysis of a coprocessing residue sample (SF 181085-2) at temperatures ranging from 685°C to 800°C was attempted in this spouted bed reactor. One of the problems with fluidized bed pyrolysis in earlier tests was the plugging of the feed injection tube due to coke formation. This problem was largely overcome with the spouted bed due to the high velocity in the spout inlet and in the spout itself. However, as was anticipated, coke and sand agglomerates accumulated in the annular region surrounding the spout. In Run 218-R a finger of coke and sand surrounded the spout like a draft tube, extending from the spout inlet to the top of the bed. In all runs, various amounts of coke accumulated in the bed, coating the sand particles and forming agglomerates.

The pyrolysis tar vapours were difficult to condense in the ice-water condensers but were removed in the front end of the cotton wool filters, which caused an increased pressure drop across the apparatus and made a constant feeding rate difficult. The appearance of the tar ranged from a viscous black tar to a light-brown powder.

9.7.2 Pyrolysis of Coprocessing Residue in a Spouted Bed

The results of four pyrolysis runs are shown in Table 9.6.

Table 9.6

Pyrolysis of Coprocessing Residues in a Spouted Bed
Sample SF 181085-2

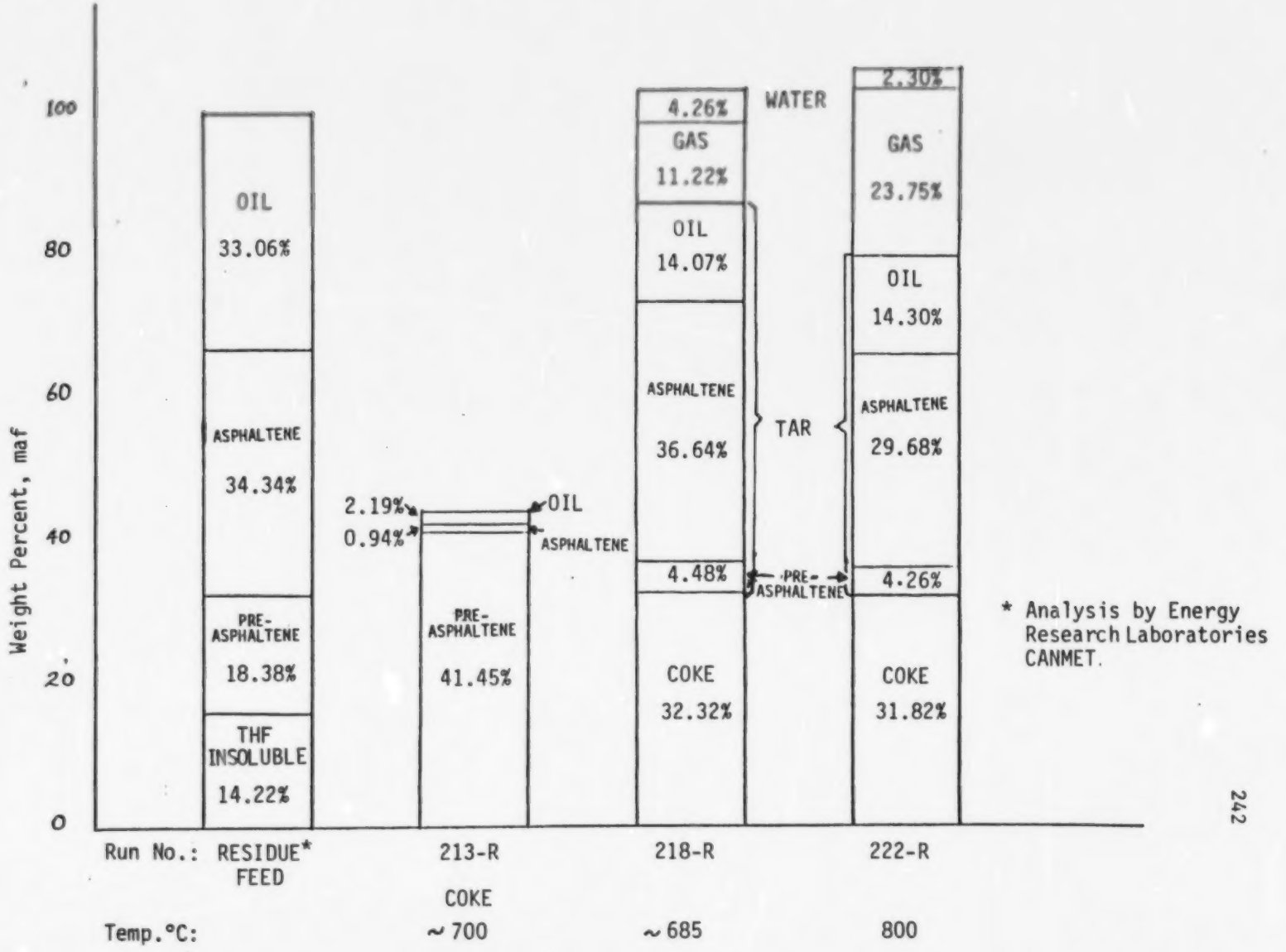
Run No.	219-R	218-R	222-R	223-R
Temperature, °C	700?	685	800	800
Residue Size, µm	-250	-250	-250	-250
Sand Size, µm	-850 +600	-850 +600	-850 +600	-850 +600
Sand Amount, g	30	60	60	40
Duration of Run, min.	18.5	16.67	19.5	12.8
Wt. of Coal Fed, g	24.65	23.79	30.71	24.62
Vapour Residence Time, s	0.24	0.21	0.19	0.19
Moisture in Feed, wt. %	0	0	0	0
Ash in Feed, dry wt. %	12.18	12.18	12.18	12.18
Ave. Feed Rate, g/h	79.9	85.6	94.5	115.4
Yields, wt. % maf				
Gas	27.37	11.22	23.75	19.16
Tar	34.32	55.19	48.24	30.39
Char	37.68	32.32	31.82	44.91
Water	2.68	4.26	2.30	2.36
Total Recovery	102.05	102.99	106.11	96.82
Yields of Gases, wt. % maf				
H_2	0.83	0.28	1.90	0.60
CO	0.81	0	1.14	0.65
CO_2	0.57	0.32	1.20	0.42
CH_4	3.85	1.72	3.84	3.75
C_2H_4	6.38	2.46	5.93	6.19
C_2H_6	0.64	0.46	0.65	0.56
C_3	3.25	1.95	3.67	2.96
C_4	2.55	1.83	2.84	1.95
C_5^+	8.51	2.20	2.60	2.08

In general, the spouted bed allowed longer run times and more residue to be fed than the fluidized bed. However, increasing pressure drop and agglomeration of the bed during a run were recurring problems. The reactor temperature was measured in the freeboard region and in the annular region of the bed for Runs 222-R and 223-R. For previous runs in the fluidized bed, only the bed temperature was measured. Because of the high gas flow rate (7 l/min @ STP) and the short mean vapour residence time (~0.2 s) in the spouted bed, a significant temperature gradient was expected as the heat flows from the hot reactor wall through the slowly mixed annular sand zone to the relatively cool spout. For both Runs 222-R and 223-R, the bed temperature decreased when feeding started due to the endothermic pyrolysis reactions of the residue. The freeboard temperature remained high. In Run 223-R the bed temperature decreased by 400°C after 5 minutes of feeding, suggesting that the spout was redirected so that it passed over the thermocouple and the low temperature measured was, in fact, the spout temperature.

Product yields, shown in Table 9.6, vary significantly for gas, tar and char. This variation is probably a result of unsteady operation and high feed rates which could result in non-uniform mixing, and non-uniform heat and mass transfer behaviour which is more pronounced in a spouted bed than in a fluidized bed. However, material balances are generally good (97% to 106%). The yields of light hydrocarbon gases are high, particularly ethylene (~6%).

Figure 9.7 shows the solvent fractionation results of the coprocessing residue and some of its products which were obtained by extraction in a soxhlet extraction apparatus. Pentane solubles were extracted for approximately 48 hours followed by toluene extraction for another 48 hours, or until the solvent became clear. For Runs 218-R and 222-R, the coke yields were about equal to the preasphaltene (toluene insoluble) and THF insoluble fraction of the residue. The coke yield was higher for Run 213-R in which the residue was fed directly into the freeboard of the fluidized bed. The asphaltene fraction of the tar of Runs 218-R and 222-R was within 5 percent of the asphaltene fraction of the residue. For Run 218-R, the oil fraction of the tar, plus the gas and water yields, were 4 percent less than the oil fraction of the residue; while the oil, gas and water from Run 222-R were about 7 percent greater than the residue oil fraction. The extra oil, gas and water of Run 222-R was produced at the expense of the asphaltene fraction, probably due to the higher reaction temperature of Run 222-R (800°C) compared to Run 218-R (685°C). It is suggested that the oil fraction and a small amount of the asphaltene fraction (probably the aliphatic component) were cracked upon pyrolysis to yield tar oils and light gases while the preasphaltene and THF insoluble fractions produced mainly coke. The asphaltene fraction did not appear to be significantly altered quantitatively. The pyrolysis coke was also found to be insoluble

FIGURE 9.7: SOLVENT FRACTIONATION OF COPROCESSING RESIDUE AND PYROLYSIS PRODUCTS



in THF suggesting that the THF soluble preasphaltenes of the residue had been further carbonized.

Figure 9.8 illustrates for the coprocessing residue the weight loss characteristics obtained by thermogravimetric analysis in CO_2. The residue and its char are not very reactive with CO_2. The reactivity measured was 0.88 g/gh maf compared with 8.46 g/gh maf for a Saskatchewan lignite under similar conditions.

9.7.3 Pyrolysis of Coprocessing Residues in a Modified Spouted Bed

Because of the improved (although still unsatisfactory) performance of the bench scale spouted bed, development of equipment and procedures for this type of reactor were continued in the evaluation of atmospheric flash pyrolysis for coprocessing residue. The initial modification to the process involved feeding the residues as a solid into a spouted bed fitted with a draft tube and collecting the tar and gas downstream. The problem of feeding the residue was no longer a limitation, and the major difficulty remaining involved the transition from the hot sticky liquid phase within the reactor to the solid coke product, which resulted in agglomeration of the coke and sand in the reactors. Several process modifications were made in an attempt to improve the operation of the runs.

One requirement for improved operation was a very consistent and dilute feed stream so that the residue in the bed remained as

same as before/950°C - 20 min

FILE: ALC01

Reactivity => 1.32 min⁻¹

CO_2 from start

REACTIVITY OF COPROCESSING RESIDUE IN CARBON DIOXIDE

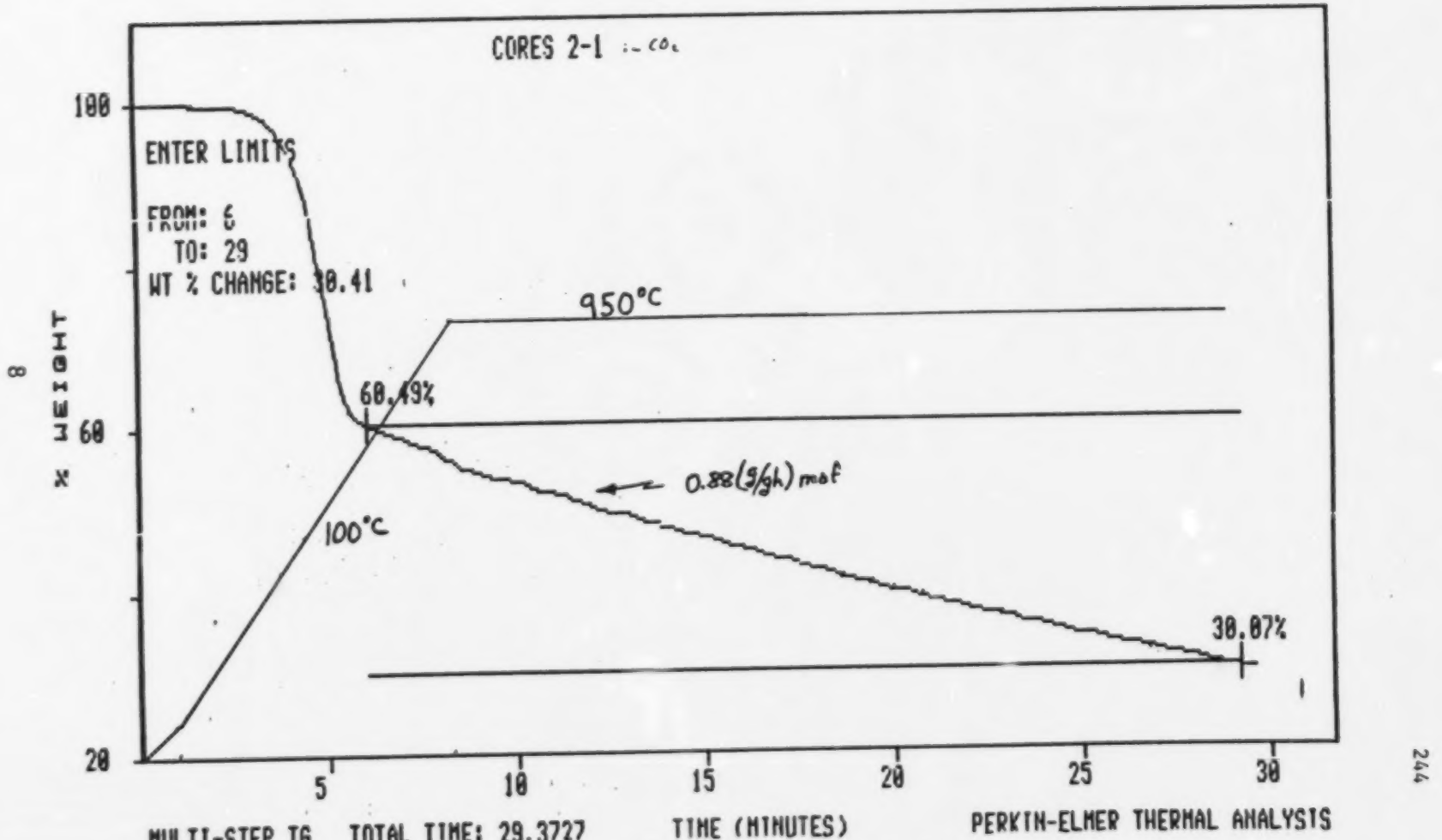


Figure 9.8 REACTIVITY OF COPROCESSING RESIDUE IN CARBON DIOXIDE

dilute as practical to avoid agglomeration. In an effort to improve the feeding characteristics the residue was frozen to reduce the stickiness, and the spouting gas was split so that only the optimal 1.5 l/min of nitrogen flowed through the feeder. These modifications were made following Run 226-R and are shown in Figure 9.9. Although feeding behaviour improved, periodic interruption of feeding followed by bursts of residue persisted. Following Run 228-R the residue was screened to remove fines (-200 mesh) which can also be a cause of high feed rates. This had little effect, if any, on the feeding behaviour.

Feed rate seemed to be very dependent on pressure fluctuations in the system. Due to the high gas rates and high velocities required to carry sand up the spout in the reactor, the pressure drop across the system was much higher than for a similar fluidized bed. Frequent variations in pressure drop occurred in the reactor and in the collection system, and these fluctuations had significant effects on the feed rates. The collection system, therefore, was also modified to remove restrictions in the tubing, which resulted in lower pressure drops across the system.

In Run 229-R a residue sample screened to -60 +140 mesh was mixed with fine (-400 mesh) Saskatchewan lignite so as to coat the residue particles with the lignite. The mixture was 17 percent coal by weight. Only 5 grams of the mixture was fed in 12 minutes (25 g/h), however, no improvement in the agglomeration problem was observed.

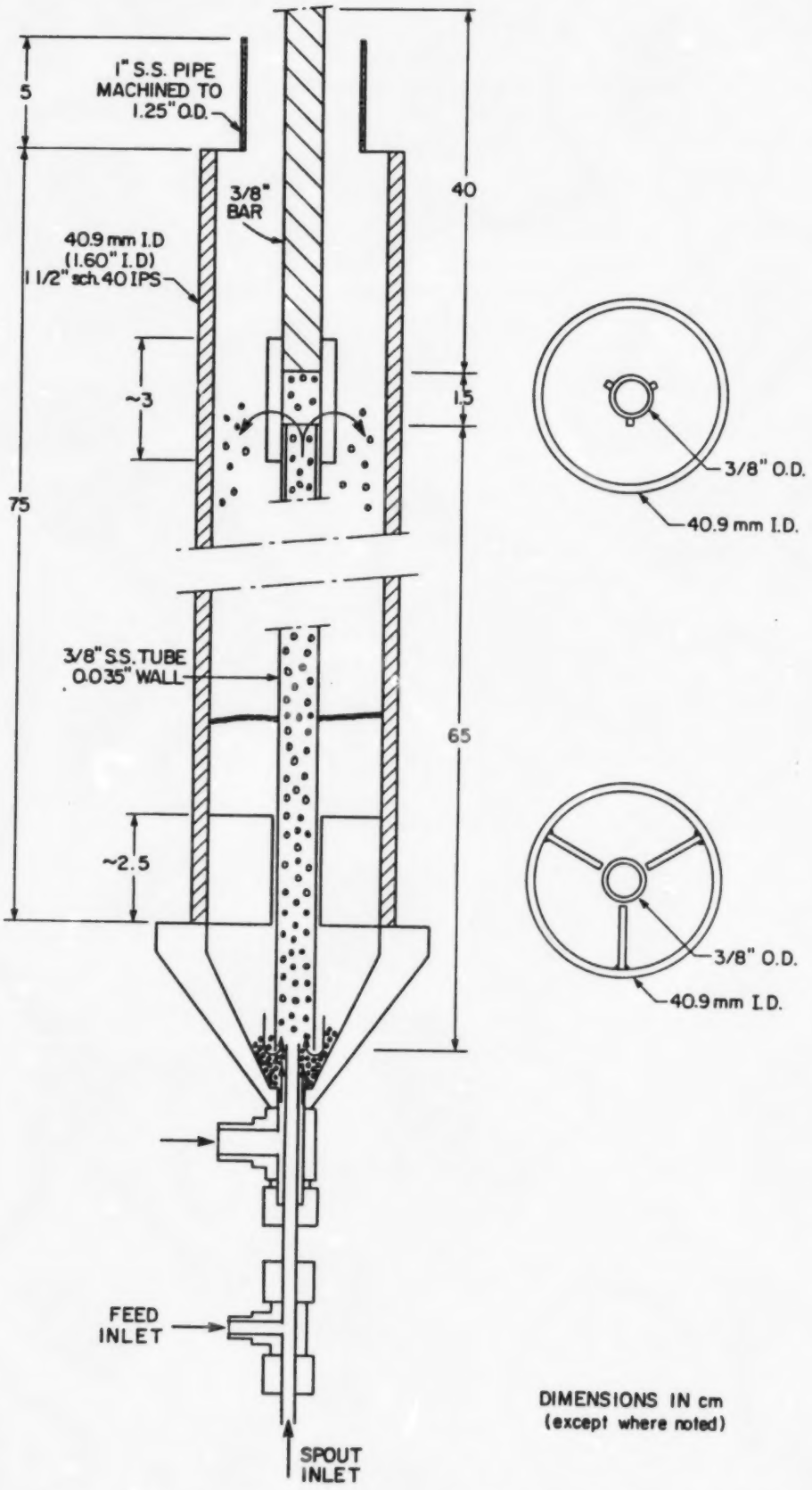


Figure 9.9 Spouted Bed Bench Scale Reactor with Internal Draft Tube

As a consequence of these tests, it seemed that a longer residence time in the high velocity zone would be beneficial, so further work focussed on the development of a larger spouted bed reactor with a draft tube similar to that described in a "Fluid Lift Solids Recirculator" by Buchanan and Wilson (26) and in a "Concentric Circulating Bed" by Fusey, Lim and Grace (27). It was hoped that the longer draft tube would achieve sufficient devolatilization of the residues in the abrasive conditions of the draft tube so that the dense products would not be tacky when they fell back with the sand into the annulus. Thus annular bed was, however, more susceptible to agglomeration problems than the draft tube because of both the fixed relationship of the sand particles to each other (that is, minimal solids agitation) and of the low gas rates.

The reactor, shown in Figure 9.9, was designed to minimize or eliminate the problems encountered with the earlier spouted bed reactor. The draft tube was suspended by a 3/8 inch diameter rod which acted as a baffle deflecting the solids down into the annulus. This eliminated carry-over of sand during the start of spouting and also minimized the accumulation of sticky material at the reactor outlet. The baffle was kept clean by the abrasive action of the spouting sand. The rod was secured by a tube fitting at the top of the reactor through which it could slide and thus the separation between the draft tube and the inlet feed tube

could be controlled. A potential problem could also develop because of the plugging of the solids entrainment area between the feed inlet and the inlet of the draft tube which would block the necessary solids circulation up the draft tube. To avoid this problem the height of the 1/8 inch inlet tube was made adjustable also allowing the tube to be raised so that it could be at the same level as the draft tube inlet. Surrounding the inlet tube at the bottom of the reactor was a concentric 1/4 inch tube which provided gas to lift the sand into the draft tube. The residue was thus immediately entrained in the relatively dilute solids flow at high velocity and subjected to the abrasive action in the draft tube.

Cold studies were done with a 50 mm diameter glass tube to determine the effects of gas rate, draft separation at the bottom, and bed depth on the solids circulation behaviour. It was observed that at zero draft tube separation and a bed depth of 100 mm, a spouting gas rate of 12.25 l/min was required to lift the sand to the top of the draft tube. Upon increasing the annular gas rate from 0 to 4 l/min the solids recirculation rate increased from near 0 to approximately 100 g/min. This solids rate was judged to be more than sufficient to accommodate the 1-2 g/min of residue fed.

In run No. 230-R, 37 grams of residue was fed, 1.4 l/min of nitrogen carried the feed with an additional 12.2 l/min of spouting gas into the draft tube. An extra 4 l/min of nitrogen in the

annular inlet lifted the sand into the spout. Assuming all the annular inlet gas (4 l/min) entered the draft tube, the gas velocity would be 19.5 m/s at 650°C and it took 0.03 seconds at 650°C to reach the top of the tube. An additional 0.54 seconds were required for the vapour to exit the reactor resulting in a total vapour residence time of about 0.57 seconds.

The high gas rates of the spouted bed relative to the fluidized bed resulted in a high pressure drop across the collection system. The high pressure drop resulted in erratic feeding characterized by slugs of residue bursting into the reactor. These slugs of residue may have been responsible for the formation of the agglomerates observed in the annular part of the bed.

The lower section of the reactor was too near the bottom of the short furnace used to reach reactor temperature, and combined with the large amount of cold gas entering the reactor may have delayed the decomposition of the residue and led to the formation of agglomerates in the annular bed of sand.

Accordingly, in subsequent tests modifications were made to raise the reactor in the furnace, pre-heat the gas and decrease the pressure drop in the collection system. It was also decided to substitute caking Balmer bituminous coal to simulate the physical behaviour of the residue in the reactor, because supplies of coprocessing residue were diminishing.

Pyrolysis yields for Run 230-R are not available as much of the vapour products were vented to minimize the pressure drop across the collection system.

9.7.4 Pyrolysis of Caking Coal in a Modified Spouted Bed

Balmer coal, a low volatile British Columbia coking coal with a free-swelling index of 4.0, was substituted as the feed material to conserve supplies of coprocessing residue. Fluidized bed pyrolysis of Balmer coal showed that it behaved in a similar fashion to coprocessing residue with respect to the agglomeration of sand in the reactor bed. The coal was already prepared and was easier to feed thus allowing maximum effort to be spent on eliminating the agglomeration problem in the reactor itself. If a system could be developed to flash pyrolyze this relatively weakly caking coal then few modifications should be required to successfully substitute the coprocessing residue for the coal.

The first run with Balmer coal incorporated the modifications described in the previous section, in that the reactor was supported higher in the furnace and the spouting and annular gases were preheated. Also because tar yields from Balmer coal are less than those of the coprocessing residue, restrictions due to tar plugging in the collection system were reduced. Reactor temperature was 650°C. Results of the run were similar to those of Run 230-R in that agglomerates formed in the annular bed of

sand and eventually stopped sand circulation. Apparently, even with gas preheating the coal was not reaching reactor temperature (650°C) in the draft tube, but was entering the relatively static annular bed in the plastic state and forming agglomerates with the sand.

In following runs, the reactor was heated to approximately 950°C in an attempt to ensure that the coal had passed through the plastic phase while in the draft tube, and that only dry char or char-coated sand would fall back into the annular bed. The run proceeded initially quite well but began to plug until gas flow ceased in both the spouting line and the annular line. Examination of the bed following the run indicated that the draft tube plugged at the feed inlet, and that the resulting diversion of gas and feed through the annular bed resulted in agglomeration of the sand at the bottom of the reactor. However, nearly 15 grams of dry char was removed from the char pot which may indicate that the reactor was operating as planned before the inlet of the draft tube became plugged. Observation of the plug showed that the feed inlet was resting against the inside wall of the draft tube as opposed to being centred. The position of the feed tube at the bottom of the draft tube is probably important to ensure that rising sand will surround the feed particles at all times and carry them upward before they can spread out to the hot walls of the draft tube.

Several modifications were made to the apparatus prior to the next pyrolysis attempt. The spouting gas requirements were checked with the open-topped reactor in the furnace at 650°C. It was found that at this temperature spouting was achieved with good sand circulation rates with only 5.6 l/min of spouting gas and 4 l/min of annular gas (@ 1 atm, 21°C). These flow rates, together with 1.4 l/min of gas through the feeder tube, resulted in draft tube velocities of 16 m/s and vapour residence times of 0.7 seconds at 650°C. Pressure gauges were connected to each of the four gas lines (spouting, annular, feeder tube, feeder top) to monitor pressure changes during a run and ultimately to obtain more knowledge of where plugging begins. Finally, the feed inlet was fitted with a spacer to centre the tube in the draft tube. Although the spacer could impede sand flow into the draft tube, this effect was not expected to be significant.

The subsequent coal pyrolysis run suffered the same fate as the previous run in that the draft tube inlet and reactor bottom became plugged with agglomerates. The draft tube plug consisted of coke only, indicating that the sand circulation to feed ratio was probably too low. Either intermittently high feed rates were overloading the draft or sand flow was restricted too much by the feed inlet spacer. The initial operating pressure of the reactor was approximately 5 psig and this increased to about 12-15 psig as the reactor became plugged.

An apparatus was assembled to test the characteristics of the feeder under 5-10 psig pressure. The feed rate was fairly consistent at approximately 60 g/h at these pressures. Sudden fluctuations in downstream pressure did result in unsteady feeding, however.

Another run with Balmer coal was attempted with particular attention to maintaining steady feeder operation. The same plugging problems were encountered, however. As feeder operation appeared to be good, it is expected that the sand circulation rate was too low.

To increase sand circulation, the bottom inlet piece of the draft tube should be enlarged to minimize restrictions to sand flow. Since the draft tube plug formed at the feed inlet it appeared that the coal was reaching pyrolysis temperatures very quickly, and therefore reactor temperature could be reduced and still maintain dry char exiting the draft tube.

9.8 CONCLUSIONS AND RECOMMENDATIONS

Heavy residues, when pyrolyzed in an inert environment at one atmosphere pressure under fast heating rate and short residence time conditions, will give good yields of hydrocarbon liquids and a dry char. Flash pyrolysis of a refinery vacuum tower residue, and of CANMET coprocessing residue (bitumen plus coal) gave good yields of a condensable tar. The coprocessing residue gave about

48%-55% tar and 30%-35% char at 685°-800°C with a vapour residence time of about 0.20 seconds. At 700°C, the refinery vacuum tower residue gave 50%-65% tar at 0.45 seconds residence time. For coprocessing residue, gas yield varied from 12% to 27%. Principal gaseous components were hydrogen and light hydrocarbons, with ethylene representing 25%-30% of the total (by weight).

The liquid product obtained from coprocessing samples pyrolyzed at 685°C and 800°C after solvent fractionation gave 25%-30% oil, 62%-66% asphaltenes and about 8% preasphaltene, which can be compared to the original coprocessing residue which had 33% oil, 34% asphaltenes and 33% preasphaltenes and insoluble residue. It appears that some of the oil fraction is cracked or gasified during pyrolysis, and the majority of the asphaltenes are recovered in the tar product, but very little of the preasphaltene fraction. Although the molecular weight of the tar was not determined, it appears to be a fluid product of reduced boiling range.

Great difficulty was experienced in achieving smooth continuous operation of the fluid bed pyrolysis reactor. These feed residues when heated pass through a sticky phase and then decompose to yield a solid coke. This coke adheres to the surfaces where it is formed, and can build up on vessel walls, feeding lines etc. to ultimately plug the reactor. The problem is compounded when using small laboratory scale reactors because of the high wall surface area to volume ratios, and the small

clearances for flow. In principle, it would be desirable in fluidized reactors to have the coke form on the sand grains without agglomeration, and there have been reports that this has been accomplished for some caking coal feeds. However, in this work, first the problem had to be solved of feeding the residues into a hot reactor without coking in the feed lines. This was finally done by using cooling together with gas or vapour as a carrier to obtain short transit times in the case of a feed which could be liquefied by heating. Granular feeds, such as the coprocessing residue, could be fed conventionally with pheumatic conveying into the bed if feed lines were short and were adequately cooled.

A number of arrangements of the fluidized bed were tried, as well as various operating techniques, but agglomeration of the sand grains always occurred, with coprocessing residues, with vacuum tower bottoms or with caking coals. Short runs could be completed to yield useful pyrolysis data, but no extended operation (over 30 minutes) could be achieved. Modifications to give a spouted core, or with a central high velocity draft tube, gave somewhat better results, but agglomeration of sand occurred ultimately whenever sand velocities were low, or sand agitation was not fairly violent.

While these experiments were not adequately successful at the bench scale level, the methods and designs used might well have

worked on a larger scale, as has been claimed by CSIRO for a spouted-fluidized bed pyrolysis unit (Smith, I.W., private communication). However, the expertise gained has suggested the criteria that must be met for successful flash pyrolysis of residues at a production level. Pyrolysis data can be gained in static systems, such as TGA, or in idealized reactors, such as the "laminar flow" transport reactor, but these are not economical designs for large throughputs.

It is recommended that the development of successful atmospheric pressure flash pyrolysis reactors for highly coking residues or coals is a goal that should be pursued. Such a reactor would find a wide range of uses for thermal reactions involving feed materials such as bitumen or coprocessing residues or coking coals which pass through a plastic stage on heating. The experiments carried out in this present study have suggested some potentially fruitful avenues for further development of this objective.

Because a good yield of oil, up to 50%, and a dry, hard char of good physical properties can be obtained from flash pyrolysis, this technology would appear to be a promising route for utilizing the large quantities of heavy residues which will exist as by-products of the liquefaction, coprocessing or upgrading processes which will become realities in the near future in Canada.

10. REFERENCES - PARTS A and B

(1) Tyler, R.J., "Flash Pyrolysis of Coals: Devolatilization of a Victorian Brown Coal in a Small Fluidized Bed Reactor", Fuel, 58, 680, 1979

(2) Scott, D.S., "Short Residence Time Pyrolysis of Coal ",Final Contract Report, DSS Contract OSU79-00190, ERL, CANMET, Ottawa, July, 1980

(3) Scott, D.S. and J. Piskorz, "A Low Rate Entrainment Feeder for Fine Solids", Ind.Eng.Chem.,Fund., 21, p.319, 1982

(4) Scott, D.S., "Screening Program on Short Residence Time Pyrolysis of Coal", Final Contract Report, DSS Contract OSU81-00087, ERL, CANMET, Ottawa, June, 1982

(5) Scott, D.S., "Screening Program on Short Residence Time Pyrolysis of Coal", Final Contract Report, DSS Contract OSU82-00255, ERL, CANMET, Ottawa, June, 1984

(6) Scott, D.S. and J. Piskorz, BIOENERGY 84, H. Egnéus and A. Ellegard (eds), Vol.III, 15-23, 1985, Elsevier Appl.Sc.Pub. (London)

(7) Earnest, C.M. and R.L. Fyans, "Recent Advances in Microcomputer Controlled Thermogravimetry of Coal and Coal Products", Thermal Analysis Appln. Study No.32, Perkin-Elmer Corp., Norwalk, CT.

(8) Scott, D.S., J. Piskorz and S. Fouda, "Pyrolysis of Low Rank Canadian Coals", Fuel Processing Technology 13, p. 157, 1986

(9) Scott, D.S., "Evaluation of the Flash Liquefaction Process Applicable to Canadian Coals", Final Contract Report, DSS Contract OST84-00007, ERL, CANMET, Ottawa, February, 1986

(10) Anthony, D.B. and J.B. Howard, "Coal Devolatilization and Hydrogasification", A.I.Ch.E.Journal, 22 (4), 625, 1976

(11) Suuberg, E.M., W.A. Peters and J.B. Howard, 17th Int. Symp. Combust., Leeds, P.117, 1978

(12) Suuberg, E.M., D. Lee and J.W. Larsen, Fuel, 64, p.1668, 1985

(13) Singla, P.K., S. Miura, R.R. Hudgins and P.L. Silveston, Fuel 62, p.645, 1983

(14) Tyler, R.J. and H.N.S. Schafer, "Flash Pyrolysis of Coals: Influence of Cations on the Devolatilization Behaviour of Brown Coals", Fuel 59, p.487, July, 1980

(15) Morgan, M.E., R.G. Jenkins and P.L. Walker,Jr., "Inorganic Constituents in American Lignites", Fuel 60, p.189, 1981

(16) Smith, J., "New Approaches to Coal Pyrolysis at CSIRO" EPRI Conference on Coal Pyrolysis, Palo Alto, Cal., February, 1981, Available from EPRI

(17) Mima, M.J., H. Schultz and W.E. McKintry, "Analytical Methods for Coal and Coal Products", Vol.1 (C. Karr, Jr., ed) Academic Press, N.Y., p.557, 1978

(18) Mijawaki, S., "Evaluation of Liquefaction Products in Flash Pyrolysis of Canadian Coals", MASc Thesis, Dept. of Chemical Engineering, University of Waterloo, Waterloo, Ontario, 1987

(19) Evans, N., T.M. Haley, M.J.Mulligan and K.M. Thomas, Fuel 65, p.694, 1986

(20) Collin, P.J., T.D. Gilbert, R.P. Philip and M.A. Wilson, Fuel 62, p.450, 1983

(21) Kube, W.R., H.H. Schobert, S.A. Benson and F.R. Karner, Fuel 65, p.39, 1984

(22) Wu, D.M.P. and D.P. Harrison, Fuel 65, p.747, 1986

(23) Tyler, R.J. and P.F. Nelson, Proc. 1985 International Conference on Coal Science, Oct. 28-31, Sydney, Australia, p.933, 1985

(24) Kandiyoti, R. and R.J. O'Brien, Proc. 1985 International Conference on Coal Science, Oct. 28-31, Sydney, Australia, p.941, 1985

(25) Kandiyoti, R., J.I. Lazarides, B. Dyrvold and C.R. Weerasinghi, Fuel 63, p.1583, 1984

(26) Buchanan, R.H. and B. Wilson, "The Fluid-Lift Solids Recirculator", Mechanical & Chemical Engineering Transactions, p.117, May, 1965

(27) Fusey, I., C.J. Lim and J.R. Grace, "Fast Fluidization in a Concentric Circulating Bed", Circulating Fluidized Bed Technology, p.409, Ed. by Prabir Basu, Pergammon Press, Toronto, 1986